

MAKING AND BREAKING OF WATER IN CRUDE OIL EMULSIONS

A Thesis

by

SHWETA D. MEHTA

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2005

Major Subject: Civil Engineering

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Approved by:

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ABSTRACT

Making and Breaking of Water in Crude Oil Emulsions.

(December 2005)

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Chair of Advisory Committee: Dr. Roy Hann Jr.

An understanding of the processes involved in oil spills, and how they interact to alter the composition and behavior of the oil with respect to time is essential to determine an effective oil spill response. The review of past research has shown more focus on the laboratory methods and computerized modeling schemes to estimate the formation and breaking of emulsions after an oil spill. However, relatively less effort has gone into the study of emulsions corresponding to actual field conditions. This research aims to simulate an oil spill at sea by developing a new technique to make water in oil emulsions, without disturbing the marine wildlife. Further, this research also attempts to analyze the viscosities of water in oil emulsions and determine appropriate emulsion breakers for different crude oil emulsions.

The overall test design for the study includes a test apparatus for spreading and evaporation, three different crude oils, a mixing chamber to form the emulsion, and emulsion breakers. Experiments in this research attempt to gain a better understanding of the processes that occur after oil spills at sea. In particular, the rate of evaporation of different crude oils and the formation of crude oil emulsions on the sea surface have been investigated. It was observed that different crude oils behave differently when subjected to the same weathering

procedure. Results indicate that the behavior of the crude oil on the sea surface, subjected to spreading, evaporation, and emulsification, can be predicted by using the new technique developed in this research. This technique can also assist the development of effective recovery equipments and materials.

DEDICATION

To my parents

ACKNOWLEDGEMENTS

I am extremely grateful to my advisor Dr. Roy Hann Jr. for his guidance, support and encouragement throughout my research and studies at Texas A and M University. Working under him, I have learned many things which will surely help in my career. I wish to thank Dr. Kramer and Dr. Parnell for serving on my committee and reviewing my work. I would also like to acknowledge and offer a big thanks to Chris Fuller, who had made all the arrangements for me at Corpus Christi for my experiments. Thanks to Dr. Barrufet in the Petroleum Engineering Department for providing me guidance and equipment to clarify my study. Thanks to Nalco Energy Services for providing me the chemicals necessary for my research.

I would like to thank my father, mother and other family members for their incessant support, encouragement and blessings throughout all these years. I owe all my success to them. Last but not the least; I specially thank my husband, Dinesh for standing by my side and being there for me, forever and always.

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CHAPTER I

INTRODUCTION

1.1 Background

Continued advances in technology have increased the demand of crude oil. As long as crude oil and other petroleum products are transported across the world's oceans, there will always be a risk of oil spill incident (Jenkins et al., 1991). In addition, pipeline blowouts, tanker loading and unloading, and other offshore industrial operations can also generate oil spills (Jenkins et al., 1991). Incidents like the Exxon Valdez and Torrey Canyon have heightened the public and government concern about environmental damages due to oil spills. People now expect oil industries to be well prepared and responsive to such emergencies (Jenkins et al., 1991).

When crude oil spills on the surface of seawater, it undergoes various biological, physical, and chemical processes, collectively known as the weathering of the oil. The weathering process includes spreading, evaporation, dissolution, dispersion, photochemical oxidation, emulsification, sinking, biodegradation, adsorption to suspended matter, and deposition on to the seafloor (Ezra et al., 2000; Mackay, 1987). Among these, the three dominant processes that change the physical characteristics are spreading, evaporation, and emulsification (Wei et al., 2003). Spreading is the most immediate and obvious process undergone by the released crude oil (Cormack, 1999).

This thesis follows the style of Journal of Petroleum Science and Engineering.

After spreading, the light volatile components of the crude oil start evaporating. The rate of evaporation depends upon the vapor pressure and the volatile components present in the crude oil (Cormack, 1999). Further, the remaining concentrated portion of crude oil mixes with the surface seawater under the influence of wind and wave action to form an emulsion (Wei et al., 2003). The emulsion formed can be either water in oil (w/o) or oil in water (o/w) emulsion as illustrated in Fig. 1. The dispersion of water droplets into the external phase of oil is called as water in oil (w/o) emulsion, while the dispersion of oil droplets in the aqueous medium/water is called oil in water (o/w) emulsion (Cormack, 1999). Water in oil emulsions may be extremely stable because the water droplets (1-10 μm diameter range) are held in a rigid structure by the components like asphaltenes, waxes, and resins (Cormack, 1999). On the other hand, oil in water emulsions are less stable because the inner droplet distance is comparatively very large and the oil droplets are relatively free to migrate (Cormack, 1999).

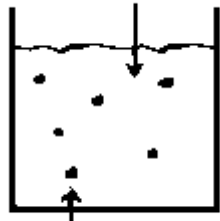
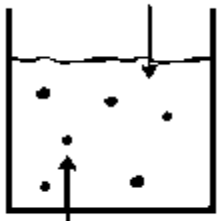
	oil in water emulsion	water in oil emulsion
Diagram	<p>external phase = water</p>  <p>internal phase = oil droplets</p>	<p>external phase = oil/fat</p>  <p>internal phase = water droplets</p>
Symbol	Oil/water o/w	water/oil w/o
Characteristics	conducts electricity, can be diluted with water	feel greasy, can be diluted with oils or solvent

Fig. 1. Difference between oil in water (o/w) and water in oil (w/o) emulsions (UBC, Vancouver, B.C., Canada V6T 1Z4)

The formation of water in the crude oil emulsion is the most important step in the weathering process because it increases the volume and viscosity of the emulsion and adversely affects the recovery and clean up. Hence, it is important to understand the processes involved in formation and breaking of w/o emulsions at the sea surface to develop an effective response system.

1.2 Problem statement

The major problem, when dealing with an oil spill is the formation of persistent water in the crude oil emulsion. The formation of such viscous emulsions increases the volume of oil residue by three to four times and makes it difficult to pump and recover (Daling, 1996).

These emulsions can have serious impacts on coastal activities by creating hazardous conditions and nuisance on the shore. Plankton, fishes, marine mammals, reptiles, and/or birds which come in contact with the w/o emulsion are at greater risk. Sometimes, the cleanup cost for an oil spill is tremendous. Exxon Corporation had to spend billions of dollars for clean up after the incident of the Exxon Valdez. Thus, the effect of an oil spill can pose both an economical and environmental threat.

In recent years, much effort has been directed towards the development of pre-spill contingency plans, response management, and clean-up equipment. Researchers are continuously investigating the process of emulsification and demulsification of crude oil to improve the response strategies. Computerized weathering models have been developed to forecast the overall fate and impact of the oil spill. However, the effectiveness of the response ultimately depends upon the type of crude oil spilled, turbulence of seawater, wind, wave action, and other sea conditions at the time of an oil spill. In order to determine the best

response system for an oil spill, a thorough knowledge of the processes involved in formation and breaking of the crude oil emulsion at sea conditions is necessary.

1.3 Research objectives

The main objective of this study is to develop a protocol to simulate the oil spill and use the best available techniques to recover the oil. For better understanding, the research objective is divided into six steps as given below:

- To build and utilize a device that allows natural spreading and evaporation of the crude oil at sea conditions.
- To build/utilize equipment to create water in oil emulsions by wave motion as it would occur at sea.
- To determine at what evaporation stages the given crude would create w/o emulsions.
- To determine the change in viscosity of the original and emulsified crude oils.
- To break the emulsions created in the above experiment and determine appropriate emulsion breakers for different crude oil emulsions.
- To develop one practical method to make and break various crude oil emulsions that is easy to use.

1.4 Organization of the thesis

Chapter II discusses the literature review. Chapter III discusses the experimental setup and methodology developed for the formation and breaking of water in oil emulsions. Chapter IV describes the results of the work. Chapter V summarizes the conclusions drawn from this empirical project and gives recommendations for future work.

CHAPTER II

LITERATURE REVIEW

Oil enters the seawater through natural seeps, accidental spills, pipeline leakage, urban runoff, wastewater discharge, industrial emissions, and other operations (Mackay and McAuliffe, 1988). Considerable effort has gone into documenting and understanding the spill incidents and estimating the adverse effects of such discharge (Mackay and McAuliffe, 1988). The basic objective of the response system is to reduce the presence of surface slicks and to avoid beach pollution (Cormack, 1999). New technologies such as boom technology, skimmers, use of surfactants to disperse the oil into small droplets, and other miscellaneous systems have emerged for controlling and treating the discharged oil (Mackay and McAuliffe, 1988). However, due to the complexities of the weathering processes and slick movement, it is difficult to predict the most efficient response technology (Daling, 1996).

2.1 Characteristics of crude oil

Crude oil is a mixture of a large amount of hydrocarbons, varying amount of waxes and low content of asphaltenes (Johansen et al., 1988). The carbon content normally is in the range of 83-87%, and the hydrogen content ranges from 10-14% (Sjöblom et al., 2002). In addition, small amounts of nitrogen, sulfur, oxygen, nickel and vanadium may be found in the crude oils (Sjöblom et al., 2002). Crude oils from different regions have different properties (Elsharkawy et al., 1995). The physical properties that mainly affect the behavior and persistence of crude oil spilled at sea are described in the following subsections.

2.1.1 Density

Density is mass per unit volume of oil and can also be expressed as specific gravity (Cormack, 1999), which is the number of times the oil is more or less dense than fresh water (density of water = 1g/ml, 1kg/l) (Cormack, 1999). All oils have specific gravity less than 1.00 with exception of some heavy crude oils (Doerffer, 1992). The American Petroleum Institute has developed the API gravity scale which expresses the ratio of weights of equal volumes of oil and pure water at a temperature of 16 °C and one atmosphere pressure (Doerffer, 1992). Generally, the dense oil is more viscous, less volatile and has high specific gravity and lower API gravity (Cormack, 1999; Doerffer, 1992).

2.1.2 Pour point

Pour point is the temperature at which the oil stops flowing and becomes semi-solid or plastic (Cormack, 1999; Doerffer, 1992). The pour point temperature is high in the oils if their wax or asphaltene content is high (Cormack, 1999). The pour point of crude oils vary from -57 °C to +32 °C (Doerffer, 1992). Lighter oils with low viscosity and density have lower pour points (Doerffer, 1992). If the pour point of the crude oil is less than the seawater, then the oil will remain liquid and disperse according to its density, viscosity and volatility, however, if the pour point is higher than the sea water it will stop flowing and be much more persistent in what is effectively the solid form (Cormack, 1999).

2.1.3 Volatility

It is the ease by which the components of the oil are lost to the atmosphere due to evaporation (Cormack, 1999). It is represented as the percentage of the total oil evaporated at different temperature ranges (Cormack, 1999). The rate and extent of loss of volatiles

depends upon surface to volume ratio and thus, the loss of volatiles increases for thin layers of oil as compared to the situation with oil in bulk (Cormack, 1999). The presence of volatile components in the early stages of the oil spill incident can increase the risk of oil combustion (Cormack, 1999).

2.1.4 Viscosity

Viscosity is the measure of the flow properties of the oil/material (Cormack, 1999). Low viscosity implies a mobile liquid and high viscosity denotes the materials that are resistant to flow, such as heavy fuel oils (Cormack, 1999). Most of the crude oils and refined products have viscosities from approximately 5 to 25000 centistokes at 15°C (Nordvik et al., 1996). Viscosity of an emulsion is governed by the factors stated below (Johnsen and Ronningsen, 2003).

- Viscosity of the continuous phase
- Viscosity of the dispersed phase
- Volume fraction of the dispersed phase
- Temperature
- Average droplet size and size distribution
- Presence of solids in addition to the dispersed phase liquid
- Shear rate
- Nature and concentration of the emulsifying agent

As the crude oil weathers, its viscosity increases due to the progressive loss of the light volatile (lower molecular weight) fractions (Doerffer, 1992). Viscosity increases with decrease in temperature (Cormack, 1999). Evaporation and emulsification increases the

viscosity of the fresh spilled oil (Cormack, 1999).

2.1.5 Flash point

The temperature at which the vapor of the oil will ignite, when exposed to an ignition source is called flash point of the oil (Doerffer, 1992). Light oils can ignite under most ambient conditions, however bunker and other heavy fuel oils do not cause a serious fire hazard when spilled on the seawater surface (Doerffer, 1992).

2.2 Behavior of crude oil on the sea surface

When the crude oil is released on the seawater surface, it undergoes certain processes, which contribute to its ultimate fate over a period. Initially, oil starts floating on the surface of the seawater at the vicinity of the point of release (Cormack, 1999). Further, it undergoes various weathering processes that alter the properties of the crude oil. The weathering process includes (Jenkins et al., 1991):

- Spreading
- Evaporation
- Dissolution
- Dispersion
- Photochemical oxidation
- Flushing due to wave energy
- Emulsification
- Microbial biodegradation
- Adsorption to suspended matter
- Sedimentation

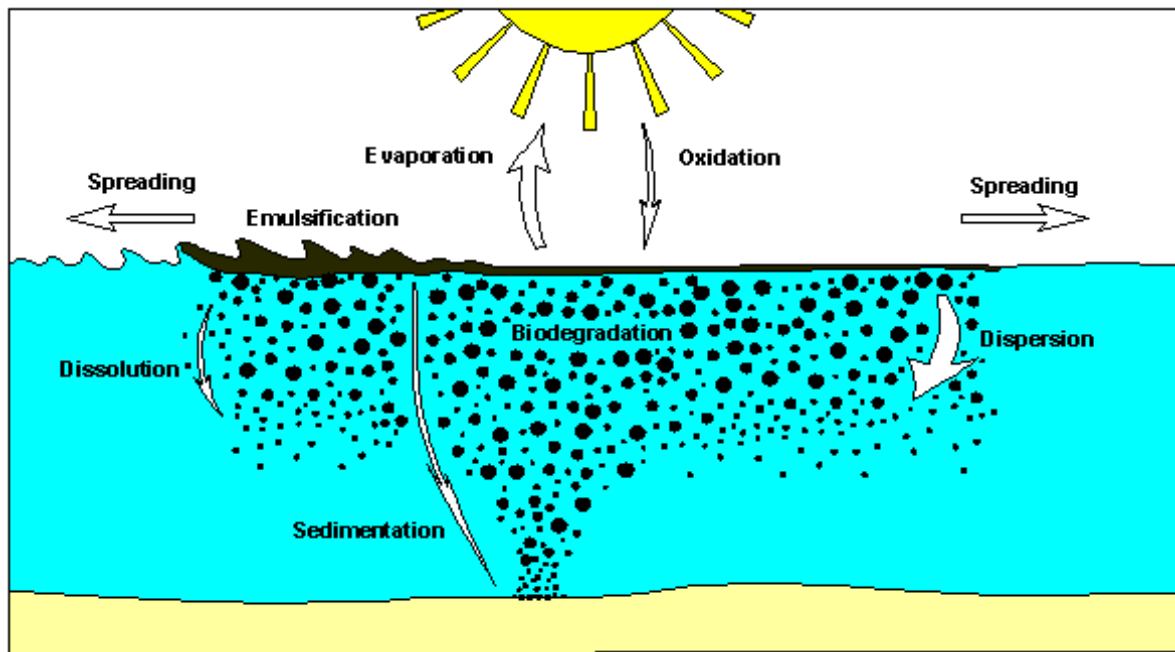


Fig. 2. Different processes responsible for the weathering of crude oil (ITOPF, 2002)

All of the processes illustrated in Fig. 2 occur simultaneously, although at different rates (Daling, 1996). The rate and extent at which these processes proceed depend on the physical and chemical properties of the crude oil (Daling, 1996). Jenkins et al. (1991) stated that spreading, evaporation and emulsification are the three processes that significantly influence the properties of the crude oil. Fundamental knowledge of these three processes is therefore necessary to predict the behavior of the spilled oil. Other processes such as photo-oxidation, microbial biodegradation, dissolution, and sedimentation also influence the behavior and fate of spilled oil, but to a lesser extent (Daling, 1996). The three important weathering processes are discussed in the following subsections.

2.2.1 Spreading

As soon as the crude oil is spilled, it starts spreading on the sea surface. The speed of spreading mainly depends upon the oil characteristics and volume of the spilled oil (Doerffer, 1992). It increases the overall surface area of the spill and enhances the mass transfer through evaporation and dissolution (Doerffer, 1992). The crude oil tends to spread to a mean thickness of approximately 0.1 mm with some thicker oil patches (Mackay and McAuliffe, 1988). The crude oil with relatively high wax contents spreads rapidly in sunlight, although at night it typically solidifies (Lee et al., 1981). Spreading behavior of crude oil is a complex process, due to the influence of various forces, interfacial tension, and sea state effects (Mackay and McAuliffe, 1988). The principal forces influencing the lateral spreading of oil on the calm sea are frictional, inertial, gravitational, and surface tension (Doerffer, J. W., 1992).

The volume of spilled oil has a direct impact on rate of spreading, because of the gravitational force, hence, large spills spread faster than small ones (Doerffer, 1992). However, the rate of spreading decreases eventually, when the surface tension becomes major spreading force (Doerffer, 1992). Surface tension decreases with increasing temperature and increases the rate of spreading (Doerffer, 1992). Light crude oils have low specific gravity and therefore great potential to spread (Doerffer, 1992).

Spreading exposes more oil to the underlying sea water and promotes dispersion of the oil into the sea by wave action (Cormack, 1999). As the crude oil mixes with seawater to form water in oil (w/o) emulsions, the rate of spreading reduces and ultimately stops due to the increase in the viscosity. This happens when there is sufficient wave motion and when the

spill is large enough (Doerffer, 1992). The thickness of the crude oil slick beyond which the spreading stops is very important as it also decreases the rate of evaporation (Reijnhart and Rose, 1982).

2.2.2 Evaporation

Evaporation is the most important weathering process during the first 24 to 48 hrs of an oil spill with regard to mass transfer and removal of light and toxic components from the spilled oil (Doerffer, 1992). Evaporative loss changes the chemical composition and physical characteristics of the crude oil (Barker and Bufarsan, 2001). These changes in composition produce changes in viscosity and density that are particularly important in controlling the behavior of an oil spill (Barker and Bufarsan, 2001). In a few days, light crude oils can lose up to 75% of their initial volumes and medium crude oils up to 40% of their volume (Fingas, 1997). However, heavy or residual crude oils will lose only about 5% of their volume in the first few days (Fingas, 1997). Reijnhart and Rose (1982) stated that the rate of evaporation depends upon various parameters like:

- oil composition and physical properties of the oil;
- wind velocity and sea condition;
- air and seawater temperature;
- the slick thickness and surface area;
- the intensity of solar radiation.

The rate and magnitude of evaporative losses depends largely on the composition of the crude oil (Reijnhart and Rose, 1982). Pervious studies have found that the initial rate of evaporation of crude oil is rapid and takes place within days, while the residue evaporation is

very slow and may take several days, weeks or months (Reijnhart and Rose, 1982). The loss of the light material by evaporation causes an increase in the viscosity and density of the crude oil (Daling, 1996). According to Doerffer, (1992), the larger the spill volume, the smaller is the evaporation rate because the surface/volume ratio of the slick thickness increases.

2.2.3 Emulsification

When the floating oil is exposed to the underlying seawater and is subjected to agitation by turbulence, it promotes the entry of water drops into the oil phase to form w/o emulsions (Cormack, 1999). Water in crude oil emulsion involves dispersion of water droplets into the continuous phase of the crude oil (Wei et al., 2003). The dispersed phase droplets are prevented from coalescing, and therefore from separating by a layer of surface-active agents present naturally in the crude oil (Pekdemir et al., 2003). The loss of volatiles during evaporation and the uptake of seawater are the two main factors that results in the formation of viscous emulsions (Cormack, 1999). The density of the resultant emulsion can be as high as 1.03g/ml (Fingas and Fieldhouse, 2003). The viscous water in oil emulsions formed are undesirable as they not only cause serious processing problems but also lead to significant cost increases for pumping, transportation, and other difficulties (Pekdemir et al., 2003). The water content in such emulsions can be as much as 60 to 70 percent in volume (Ronningsen, 1992). Thus, emulsification is a major weathering process, which not only increases the volume of the pollutants but also renders the oil much more viscous than the original oil released (Cormack, 1999).

2.3 Formation and stability of water in oil emulsions

An emulsifying agent must be present to form stable water-in-crude oil emulsions (Sjöblom et al., 2002). Such agents include clay particles, added chemicals or the crude oil components like asphaltenes, waxes, resins and naphthenic acids (Sjöblom et al., 2002). The mechanism of emulsification was poorly understood until the 1990's (Fingas and Fieldhouse, 2003). The basic physics of water-in-oil emulsification was understood in the surfactant industry, but not in the oil spill industry (Fingas and Fieldhouse, 2003). In the late 1960's, Berridge and his co-workers were the first to measure several physical properties of emulsions (Fingas and Fieldhouse, 2003). They described the formation of emulsions due to the asphaltene and resin content of the oil (Fingas and Fieldhouse, 2003). Mackay and McAuliffe (1988) also stated that the main factors affecting the stability of the emulsion is the presence of substances like crude oil resins, asphaltenes, and natural wax.

Resins are comprised of polar molecules often containing hetero-atoms such as nitrogen, oxygen or sulfur. It is defined as the fraction of crude oil soluble in light alkanes like pentane and heptane, but insoluble in liquid propane (Sjöblom et al., 2002). Asphaltenes are polar molecules similar to the resins, but with higher molecular weight, typically 500-1500 g/mole (Sjöblom et al., 2002). Asphaltene are defined as the fraction of the crude oil precipitating in light alkanes like pentane, hexane, and heptane (Sjöblom et al., 2002). It was found that asphaltenes were a major factor in emulsion stability (Fingas and Fieldhouse, 2003).

Asphaltene fraction contains the highest percentage of hetero-atoms (O, S, and N) and organometallic constituents (Ni, V, Fe) in the crude oil (Sjöblom et al., 2002). These components combine with organic and/or inorganic solids producing emulsion-stabilizing

films at oil-water interface, and contribute to the formation of stable emulsions (Cormack, 1999). Refined petroleum products do not contain asphaltenes and waxes and hence they do not form stable emulsions (Doerffer, 1992). In 1992, Schramm and his co-workers provided the oil spill industry with the basic understanding of water-in-oil emulsions (Fingas and Fieldhouse, 2003).

The most important characteristic of a water-in-crude oil emulsion is its stability (Fingas and Fieldhouse, 2003). Water in oil emulsions made from crude oils have different classes of stability, due to the presence of asphaltenes and resins (Fingas and Fieldhouse, 2004). The four classes of stability are: stable, meso-stable, unstable, and entrained water (Fingas and Fieldhouse, 2004). These four classes can be differentiated by visual appearance as well as by rheological measurements (Fingas and Fieldhouse, 2003). Out of these four states, only stable and meso-stable states can be characterized as emulsions (Fingas and Fieldhouse, 2004). Stable emulsions increase their viscosity with time (Fingas and Fieldhouse, 2003). It is suspected that the stability derives from the strong visco-elastic interface caused by asphaltenes and resins (Fingas and Fieldhouse, 2003). Mesostable emulsions are the emulsions between stable and unstable emulsions (Fingas and Fieldhouse, 2004). It is thought that meso-stable emulsions lack sufficient quantities of asphaltenes to render them completely stable (Fingas and Fieldhouse, 2004). The meso-stable emulsions may degrade to form layers stable emulsions (Fingas and Fieldhouse, 2003). The color of the meso-stable emulsions can be red or black (Fingas and Fieldhouse, 2003). Unstable emulsions are those that decompose to water and oil immediately after mixing (Fingas and Fieldhouse, 2003). Sometimes water may be retained by the oil, especially if the oil is viscous (Fingas and

Fieldhouse, 2003). The unstable emulsions do not show the same increase in viscosity as the stable emulsions (Fingas and Fieldhouse, 2003).

For most of the emulsions, it is observed that the emulsion stability decreases with increasing temperature, because at high temperatures the viscosity of the continuous phase decreases with the increase in the rate of collision of dispersed phase droplets (Cormack, 1999). Stable emulsions can have 20 to 80% water content, which may be in the form of small droplets, but when temperature increases, coalescence is enhanced and ultimately there is phase separation (Cormack, 1999). Therefore, the formation and stability of the emulsions largely depends upon the temperature, sea conditions and the presence of natural components like asphaltenes, waxes, and resins (Lane, 1995).

2.4 Breaking of water in crude oil emulsions

The emulsions formed on the sea after oil spills are inherently stable. Emulsion breaking is one of the most complex processes in the oil industry. Breaking of water in crude oil emulsions involves chemical, thermal, electrical, or a combination of these processes depending on the characteristics and properties of the emulsion (Mohammed et al., 1993). Various methods of demulsification, like centrifugation, sedimentation, heating, use of dispersants and emulsion breakers have been examined (Kim et al., 2002). Amongst these techniques, heating and centrifugation did not gain much acceptance due to the high cost and energy requirements. The realization that dispersants cannot deal with higher viscosity emulsions, encouraged the investigation of the possible application of emulsion breakers (Cormack, 1999). The addition of chemical demulsifiers in small quantities can greatly facilitate oil-water separation (Poindexter and Lindemuth, 2004). According to Nordvik et al.

(1996), the main advantages of using emulsion breakers are:

1. Rapid and cost effective
2. Reduction in the viscosity of crude oil emulsions
3. Improve pump-ability
4. Reduce oil waste handling
5. Reduces the final disposal cost by a factor of 10.

Breaking of such emulsions also requires introduction of some turbulent energy (Lane, 1995). The energy requirement is variable and depends upon the type of energy induction and the type of emulsion breaker used (Lane, 1995). The main objective of the emulsion breaker/demulsifier is to displace the naturally occurring emulsifying agents from the oil-water interface (Cormack, 1999). Nordvik et al. (1996) stated that the efficiency of the emulsion breakers depends upon:

1. The efficiency of the product (emulsion breaker)
2. Oil characteristics
3. Environmental conditions
4. Application method
5. Time of application

Emulsion breaking must be attempted at the earliest possible opportunity in the oil spill response process (Cormack, 1999). Lots of different emulsion breakers are available in the market and the choice of the most efficient one is a time consuming and difficult process. Therefore, different emulsion breakers are generally tested through a bottle test method,

which consist of adding the given emulsion breaker to the sample of the emulsion and observing the percentage of water as function of time (Goldzal and Bourrel, 2000).

CHAPTER III

EXPERIMENTAL METHODS

This research has developed a new technique to form the crude oil emulsions as they are formed on the sea and further break those by using a suitable, commercially available emulsion breaker. Three different crude oils (Arabian medium, Kuwait and Louisianan) were used for the experiment. A series of experiments were carried out to determine the behaviors of these three different crude oils when subjected to evaporation, emulsification, and demulsification. For a better understanding of the research, the experimental procedure was divided into four steps:

- Spreading and evaporation of the crude oil
- Formation of water in crude oil emulsions
- Evaluating the viscosities of the emulsions
- Breaking of the water in crude oil emulsions

The experiment faced a variety of challenging issues in order to maintain a realistic simulation of the oil spill in the natural environmental conditions. One of those challenges was to find a location for the experimental oil spill study that would be acceptable in terms of permitting and would match the sea conditions. The other challenges include the simulation of the wave action, simulating the formation of emulsions.

3.1 Spreading and evaporation of crude oil

Equipment that allows simultaneous spreading and evaporation of the crude oil was designed and constructed. The apparatus essentially consists of a spreading device and a corrugated

plate, supported by angle irons in the form of a framework as shown in Fig. 3. A 10 gage galvanized corrugated iron sheet was used in the experiment to simulate the wave action.



Fig. 3. Experimental setup for spreading and evaporation of the crude oil.

The corrugated plate was inclined at an angle of 60° to maintain a continuous flow of crude oil, as shown in Fig. 4. A peristaltic pump with flexible tubing was used to pump the crude oil from the container and deliver it on to the spreading device. The spreading device was positioned at the top of the corrugated plate to sustain a continuous and smooth flow of crude oil over the corrugated plate. The basic concept was to circulate the crude oil evenly over the $3.2' \times 1.5'$ corrugated plate to achieve natural spreading and evaporation of oil. The detailed illustration of the continuous flow cycle of crude oil is as shown in Fig. 4.

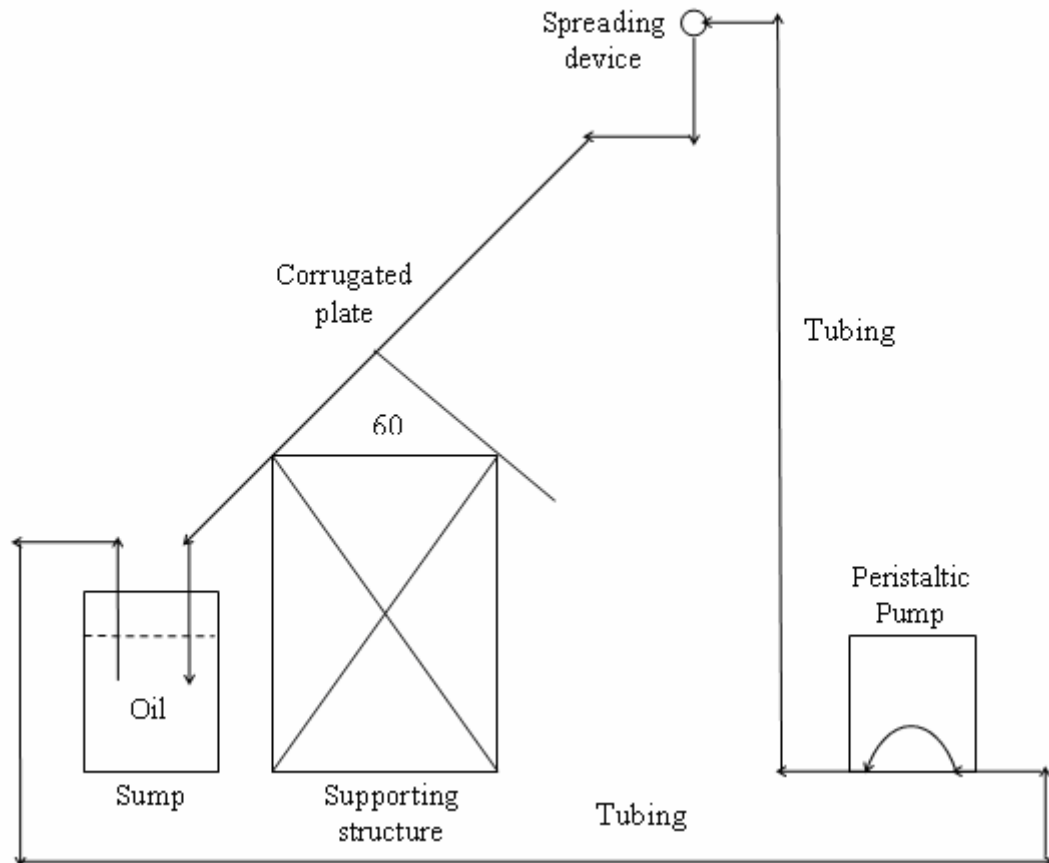


Fig. 4. Schematic representation of the cyclic flow path of crude oil

The peristaltic pump that was used to maintain a continuous circulation of the crude oil is shown in Fig. 5. The front casing of the peristaltic pump consists of flexible tubing fitted over rollers. When the pump is started, the rollers compress the tubing which forces the crude oil to move through the tube and enter the spreading device. The change in the direction of rotation will result in the change in the direction of the flow.

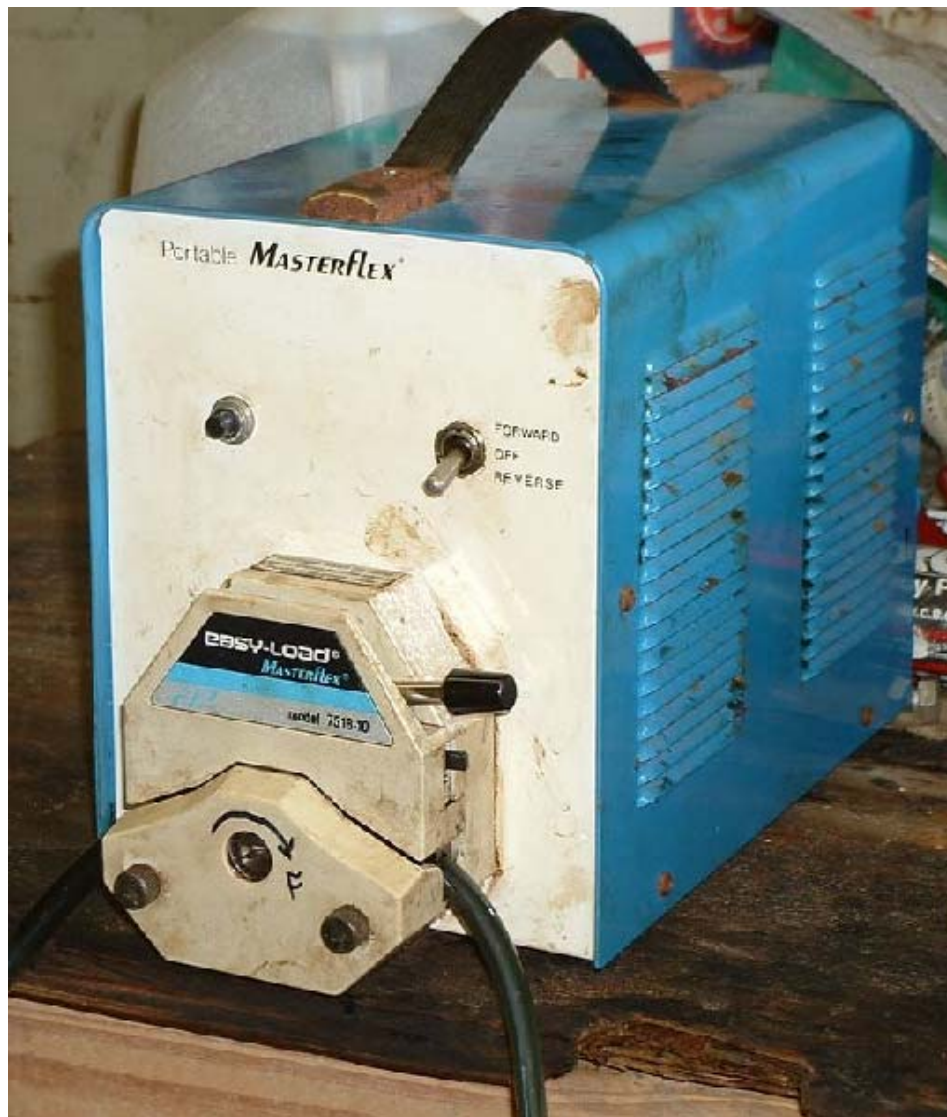


Fig. 5. Peristaltic pump (Cole Palmer)

As shown in the Fig. 4, the oil coming from the peristaltic pump enters the spreading device. A plastic pipe with 12 holes, each of 0.30 centimeter diameter was mounted on the top of corrugated plate, which served as the spreading device. The main purpose of the spreading device was to deliver the oil uniformly over the surface of the corrugated plate. The operation of the spreading device is displayed in Fig. 6.



Fig. 6. Spreading device mounted at the top of corrugated plate

After spreading over the corrugated plate, the crude oil was collected in the same container, from where it was again pumped and re-circulated, as shown in Fig. 7.



Fig. 7. Arrangement made to collect the crude oil coming from the corrugated plate.

A trial experiment was conducted with water to check the efficiency of the equipment. Initially, c-flex tubing (1/4th inch inner diameter, 3/8th inch outer diameter) was used for the circulation. However, due to the sliding friction, the rollers of the peristaltic pump eroded the tubing in a few hours. Later, a vinyl tubing of same dimensions (max psi = 60psi at 68F) was used, which showed better results than the earlier tubing.

All of the field experiments in this research were carried out at SERF, Corpus Christi to achieve the natural sea conditions. SERF is the Shoreline Environmental Research Facility of Texas A and M University at Corpus Christi. Once the experimental apparatus was set up,

the actual experiment with the crude oils was started. Crude oil was continuously circulated over the surface of the corrugated plate at the rate of 0.8 liter/min. The time required for 10%, 20%, and 30% evaporation of all the three crude oils (Arabian medium, Kuwait and Louisiana) was measured at standard test conditions. Evaporation was determined in terms of volume loss throughout the experiment. This experiment was carried out in the natural environmental conditions to imitate the sea conditions. Samples of all the three crude oils at different stages of evaporation were collected and stored for future studies and experiments.

3.2 Formation of emulsions

The oil samples collected at different stages of evaporation (10%, 20%, and 30%) were mixed individually with salt water in the mixing chamber. A small commercially available cement mixer was found to have all the features desired and was chosen as the mixing chamber. While mixing, the cement mixer was covered with a plastic sheet to avoid evaporative losses and oil spillage as shown in the Fig 8. The ratio of crude oil to salt water was 1:2. The salt water used in the experiment to make the emulsions, was readily available at SERF, Corpus Christi. The salt water had salinity of approximately 27 ppt (parts per thousand). The idea of using a cement mixer for making emulsions was successful, but took a considerable amount of time. A faster method was found using a regular kitchen blender. The rigorous speed of the blender allowed rapid emulsification. Again, the same procedure was repeated for all the three oils. The samples of the emulsions formed by the mixing chamber as well as by the regular kitchen blender were stored in glass jars for about a week to confirm the stability.



Fig. 8. Mixing chamber

3.3 Evaluating viscosities

After the formation of the water in crude oil emulsions, the next step in the research was to evaluate the viscosity of the emulsions. It is essential to determine the viscosities of the emulsions to develop efficient pumping and other recovery equipment. Viscosities of the water in crude oil emulsions were characterized by using a Brookfield digital rheometer (model III) in centipoise (cp).

3.4 Breaking of emulsions

The emulsion breaker (EC2003A) was selected based upon the types of crude oils and guidelines provided by Nalco Energy Chemicals (Sugarland, Texas). The main contents of the emulsion breakers are methanol, aromatic naphtha, and naphthalene derivatives. The procedure recommended by Nalco to break the water in crude oil emulsions used in this experiment was as follows:

1. Obtain a chemical free sample of the water in oil emulsion, prepared earlier in the experiment.
2. Fill a bottle to 100 ml level with the emulsion, cap it, and invert to coat the glass with an emulsion film.
3. Add 100 ppm of the demulsifier, EC2003A to the emulsion.
4. Agitate the bottle by shaking 100 times by hand to disperse the chemical into the emulsion.
5. Observe and record the time required for the separation of crude oil and seawater.
6. Repeat the same procedure for the other two samples of emulsions.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Spreading and evaporation of crude oil

To simulate an oil spill, three different crude oils (Arabian medium, Kuwait, and Louisiana) were subjected to natural spreading and evaporation by continuously circulating them over the corrugated plate. The volume loss of the crude oil was measured with respect to time.

Tables 1, 2, and 3 summarize the total number of hours required for evaporation of Arabian medium, Kuwait, and Louisiana crude oil respectively.

Table 1

Arabian medium: 10 % natural evaporation with respect to time.

Oil type	Temperature (° F)	Humidity (%)	Container Depth (Inches)	Time (Hrs)
Arabian medium	71.0	59	11.2	0:00
Arabian medium	63.3	87	10.6	3:46
Arabian medium	65.0	88	10.45	5:20
Arabian medium	65.5	100	10.1	7:00

Two quarts of 10% evaporated oil was taken for sample. Hence, the depth of the container lowered from 10.1 to 9.65

Arabian medium: 20 % natural evaporation with respect to time.

Arabian medium	65.5	100	9.65	7:00
Arabian medium	71.8	79	9.1	10:09
Arabian medium	68.7	100	8.85	13:36
Arabian medium	68.0	100	8.7	17:21

Two quarts of 20% evaporated oil was taken for sample. Hence, the depth of the container lowered from 8.7 to 8.25

Arabian medium: 30 % natural evaporation with respect to time.

Arabian medium	73.6	81	8.25	17:21
Arabian medium	81.7	66	8.0	21:06
Arabian medium	71.4	84	7.75	26:54
Arabian medium	69.1	100	7.65	33:00
Arabian medium	80.4	70	7.55	39:10
Arabian medium	74.3	82	7.4	44:25

Table 2

Kuwait crude oil: 10 % natural evaporation with respect to time.

Oil type	Temperature (° F)	Humidity (%)	Container Depth (Inches)	Time (Hrs)
Kuwait crude	76.0	88	12.1	0:00
Kuwait crude	69.3	100	11.1	4:00
Kuwait crude	72.0	81	11.1	4:30
Kuwait crude	76.0	81	10.9	6:00

Two quarts of 10% evaporated oil was taken for sample. Hence, the depth of the container lowered from 10.9 to 10.45

Kuwait crude oil: 20 % natural evaporation with respect to time.

Kuwait crude	76.0	81	10.45	6:00
Kuwait crude	82.6	72	10.3	9:05
Kuwait crude	91.8	68	10.0	12:20
Kuwait crude	71.0	83	9.4	18:20

Two quarts of 20% evaporated oil was taken for sample. Hence, the depth of the container lowered from 9.4 to 8.95

Kuwait crude oil: 30 % natural evaporation with respect to time.

Kuwait crude	70.0	70	8.95	18:20
Kuwait crude	75.0	88	8.6	25:05
Kuwait crude	84.4	70	8.45	31:10
Kuwait crude	78.0	96	8.25	36:10
Kuwait crude	86.2	66	8.20	42:10
Kuwait crude	78.0	72	8.05	48:10

Table 3

Louisiana crude oil: 10% natural evaporation with respect to time.

Oil type	Temperature (° F)	Humidity (%)	Container Depth (Inches)	Time (Hrs)
Louisiana crude	76.0	75	12.1	0:00
Louisiana crude	82.8	66	11.2	2:45
Louisiana crude	83.5	63	10.9	3:30

Two quarts of 10% evaporated oil was taken for sample. Hence, the depth of the container lowered from 10.9 to 10.45

Louisiana crude oil: 20 % natural evaporation with respect to time.

Louisiana crude	83.5	73	10.45	3:30
Louisiana crude	76.5	72	9.8	9:15
Louisiana crude	74.5	91	9.7	11:15
Louisiana crude	84.9	62	9.4	16:45

Two quarts of 20% evaporated oil was taken for sample. Hence, the depth of the container lowered from 9.4 to 8.95

Louisiana crude oil: 30 % natural evaporation with respect to time.

Table 3 (Continued)

Oil type	Temperature (° F)	Humidity (%)	Container Depth (Inches)	Time (Hrs)
Louisiana crude	84.9	62	8.95	16:45
Louisiana crude	77.0	62	8.95	20:30
Louisiana crude	74.0	84	8.6	33:30
Louisiana crude	98.7	61	8.4	39:00
Louisiana crude	90.0	90	8.3	42:00
Louisiana crude	95.0	92	8.05	49:30

Note: 20 % evaporation is considered as 10% of 10% already evaporated oil and not direct 20% evaporation of un-weathered oil. It is also the same with 30 % evaporation.

The following pictures display the original un-weathered oil samples and the samples collected after 10%, 20%, and 30% evaporation of all the three crude oils



Fig. 9. Samples of un-weathered, 10% evaporated, 20% evaporated and 30% evaporated Arabian medium crude oil. (From left to right)



Fig. 10. Samples of un-weathered, 10% evaporated, 20% evaporated and 30% evaporated Kuwait crude oil. (From left to right)



Fig. 11. Samples of un-weathered, 10% evaporated, 20% evaporated and 30% evaporated Louisiana crude oil. (From left to right)

The crude oil samples displayed in the fig 9, 10, 11, look quite similar, but in real have extremely different viscosities. It was observed that the viscosities increase with increase in the rate of evaporation.

The evaporation times observed for all the crude oils approximately match the output from ADIOS model (as shown in Appendices A, B, C, and D).

4.2 Formation of emulsions

After evaporation, each oil sample displayed above in figures 9, 10, and 11, was mixed with salt water (salinity of 27 ppt) in the mixing chamber (cement mixer) for 24 hours to create emulsions. Further, to obtain viscous emulsions, these emulsions were mixed in the regular blender. The pictures below demonstrate the difference in the physical appearance of the emulsions prepared by the mixing chamber and the emulsions prepared by a regular blender. The figures also indicate the correlation between the rate of evaporation and the stability of the water in crude oil emulsions.



Fig. 12. Arabian medium crude oil emulsions prepared by using mixing chamber for 24 hrs reflect correlation between the evaporation rate and the stability of the emulsions.



Fig. 13. Arabian medium crude oil emulsions (chocolate mousse) prepared by using regular blender



Fig. 14. Kuwait crude oil emulsions prepared by using mixing chamber for 24 hrs reflect the correlation between the evaporation rate and the stability of the emulsions.



Fig. 15. Kuwait crude oil emulsions (chocolate mousse) prepared by using regular blender



Fig. 16. Louisiana crude oil emulsions prepared by using mixing chamber for 24 hrs, reflect the correlation between the evaporation rate and the stability of the emulsions.



Fig. 17. Louisiana unstable emulsions prepared by using regular blender

Observations made on the appearance of the crude oil emulsions as seen in figures 12, 13, 14, and 15 show that for the Arabian medium and Kuwait crude oils, the stability increases with the rate of evaporation. These two crude oils had tolerable viscosities originally; however it was observed that their viscosities increased rapidly with emulsion formation. Significant changes in the physical properties of the crude oil were observed when these crude oils were subjected to evaporation and emulsification. Figs. 16 and 17 indicate that the stability was not affected by evaporation for the Louisiana crude oil. All the stable emulsions appeared to be brown, viscous, and remained unbroken for over two weeks. However, the non stable emulsions broke down into water and oil within a week. In some emulsions, the entrained water appeared to be in the form of large suspended water droplets.

4.3 Evaluating viscosities

The viscosities of the crude oils and their emulsions were determined by using a Brookfield digital rheometer. The following Tables 4 and 5 illustrate the viscosity of the starting oil and the change in viscosity due to evaporation and emulsification, respectively.

Table 4
Viscosities of the evaporated crude oils

Oil type	Evaporation (%)	Viscosity (cp)
Arabian Medium	0	10.9
Arabian Medium	10	22.1
Arabian Medium	20	42.0
Arabian Medium	30	149.0
Kuwait	0	6.27
Kuwait	10	15.8
Kuwait	20	40.6
Kuwait	30	192.0
Louisiana	0	3.00
Louisiana	10	5.73

Table 4 (Continued)

Oil type	Evaporation (%)	Viscosity (cp)
Louisiana	20	8.73
Louisiana	30	13.6

Table 5

Viscosities of the crude oil emulsions (chocolate mousse)

Oil type	Evaporation (%)	Viscosity (cp)
Arabian Medium	0	9262
Arabian Medium	10	10429
Arabian Medium	20	13125
Arabian Medium	30	13246
Kuwait	0	2016
Kuwait	10	2351
Kuwait	20	2567
Kuwait	30*	19796
Louisiana	0	184
Louisiana	10	186
Louisiana	20	193
Louisiana	30	240

* shows the highest viscosity because the emulsions were mixed in the mixing chamber for nonstop seven days, which shows that this mixing chamber and procedure used in this experiment works well, although it takes more time.

4.4 Breaking of emulsions

The last step in the research was to break the crude oil emulsions. The emulsion breaker EC2003A recommended by Nalco Energy Services was added to each crude oil emulsion sample at standard conditions. The detailed procedure followed for emulsion breaking is described in Section 3.4. After agitating the emulsions with the emulsion breaker for about 100 times, the mixture was allowed to settle for approximately 2 minutes. Within this time clear separation of crude oil and water was observed for all three oil samples. Figure 18 illustrates this separation.



Fig 18. Oil water separation by addition of emulsion breaker EC2003A

CHAPTER V

SUMMARY AND CONCLUSION

The main idea of this research was to spread, evaporate, and emulsify the crude oil in a natural environment to simulate an oil spill. Further, an attempt was made to break these emulsions by using a commercially available emulsion breaker. The experimental procedure includes designing and building of an apparatus which mainly consisted of a corrugated plate to simulate the wave action of the ocean/sea. The crude oil was circulated continuously over the corrugated plate with the help of a peristaltic pump to achieve weathering of the oil. Three different crude oils (Arabian medium, Kuwait, and Louisiana) were used in this experiment. The time required for natural evaporation of the crude oils was measured and is summarized in the table 6.

Table 6
Time required for natural evaporation

Crude oil	Time required for 10% evaporation (Hours)	Time required for 20% evaporation (Hours)	Time required for 30% evaporation (Hours)
Arabian medium	7	17:21	44:25
Kuwait	6	18:20	48:10
Louisiana	3:30	16:45	49:30

The above table shows that for all the three crude oils the rate of evaporation is initially high, however later it decreases as the evaporative losses produce a residual crude oil with increased density and viscosity. This apparatus can also be used in the future studies and

researches to determine the natural rate of evaporation of various crude oils when spilled on the sea.

In the next step of the research a commercially available cement mixer was used as the mixing chamber to create water in oil emulsions. The mixer was selected on the basis of the following:

- The motion of the mixer replicates the wave action of the ocean/sea.
- It was easy to load and unload the seawater, crude oil, and emulsions.

It was observed that emulsions were formed slowly in the mixer, whereas stable emulsions (chocolate mousse) were rapidly formed by using a regular kitchen blender. However, the high speed of the blender creates small water droplets in the emulsions; this is not analogous to the emulsions formed on the sea after an oil spill. Further investigation is needed to improve the features of the mixer (e.g. increasing the number of baffles in the mixer) and utilize it as a realistic technique to form water in oil emulsions.

After 24 hours of mixing in the mixing chamber, the emulsions of Arabian medium and Kuwait crude oils displayed different levels of stability depending upon the rate of evaporation as shown in Figs. 12 and 14. However, being light this was not observed in the case of Louisianan crude oil (Fig 16). This shows that the behavior of the crude oil on the sea ultimately depends on the physical and chemical properties of the crude oil itself.

Finally, the experimental work conducted in this research demonstrates the important role of an emulsion breaker after an oil spill. It was observed that the commercially available

emulsion breaker (EC2003A - Nalco Energy Services) could quickly and efficiently separate water from crude oil for all the three crude oil emulsions.

In the absence of a reliable method to predict the behavior of spilled oil, the empirical technique developed in this research to spread, evaporate, and emulsify the crude oils, can provide relevant and useful information to make decisions about the oil spill response strategies. Researchers can use this technique as a protocol for understanding the behavior of different crude oils spilled on the sea. Therefore, the potential use of this research in future oil spill studies related to crude oil emulsions is significant.

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APPENDIX A

ADIOS MODEL – ARABIAN CRUDE OIL

The findings of this research were compared with the output of the ADIOS model. ADIOS (Automated Data Inquiry for Oil Spills) model is an initial oil spill response tool, for oil spill responders. ADIOS calculations are based on various assumptions like oil spill is unhindered, use of only one emulsification constant for all types of crude oils, use of a constant temperature throughout the oil spill, etc. These estimates may sometimes impact the output and the ADIOS results may be inaccurate.

The rate of evaporation, viscosity, density and water content of all the three crude oils (Arabian medium, Kuwait and Louisiana) were calculated by the ADIOS software. The ADIOS software worked such that:

Input:

- oil type,
- wind speed,
- water temperature, and
- the oil release information.

Output (Graphs):

- Oil evaporation (%) with respect to time,
- Viscosity in cP,
- Viscosity in cSt,
- Density, and

- Water content.

It was observed that the rate of oil evaporation (%) calculated by the ADIOS model went parallel with those calculated by the empirical technique in this research. The output of the ADIOS software for Arabian medium, Kuwait and Louisiana crude oils are displayed in Appendix A, B and C respectively. Appendix D consists of some brief notes and information regarding the output graphs given by ADIOS.

Spill Scenario

ADIOS® 2.0



- **Oil Type**

- ARABIAN MEDIUM, EXXON

- Location = SAUDI ARABIA

- Synonyms = none listed

- Product Type = crude

- API = 30.0

- Pour Point = -23 deg C

- Flash Point = unknown

- Viscosity = 11.7 cSt at 38 deg C

- Adhesion = unknown

- Aromatics = unknown

- **Wind and Wave Conditions**

- Wind Speed = 13 mph from 55 degrees

- **Water Properties**

- Temperature = 60 deg F

- Salinity = 27 ppt

- Sediment Load = 5 g/m3 (ocean)

- Current = 0 mph

- **Release Information**

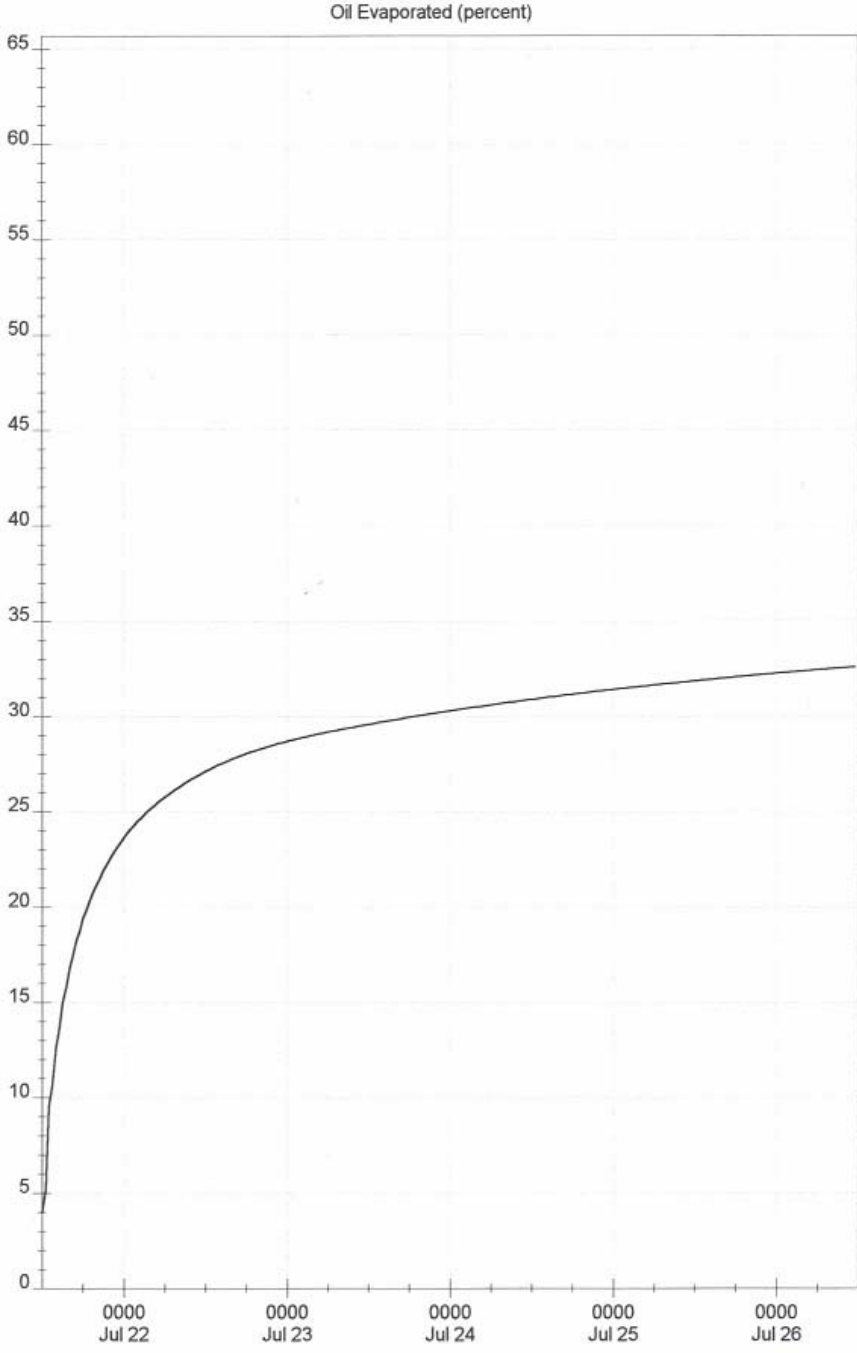
- **Instantaneous Release**

- Time of Release = July 21, 1200 hours

- Amount Spilled = 10000 bbl

Spill Scenario

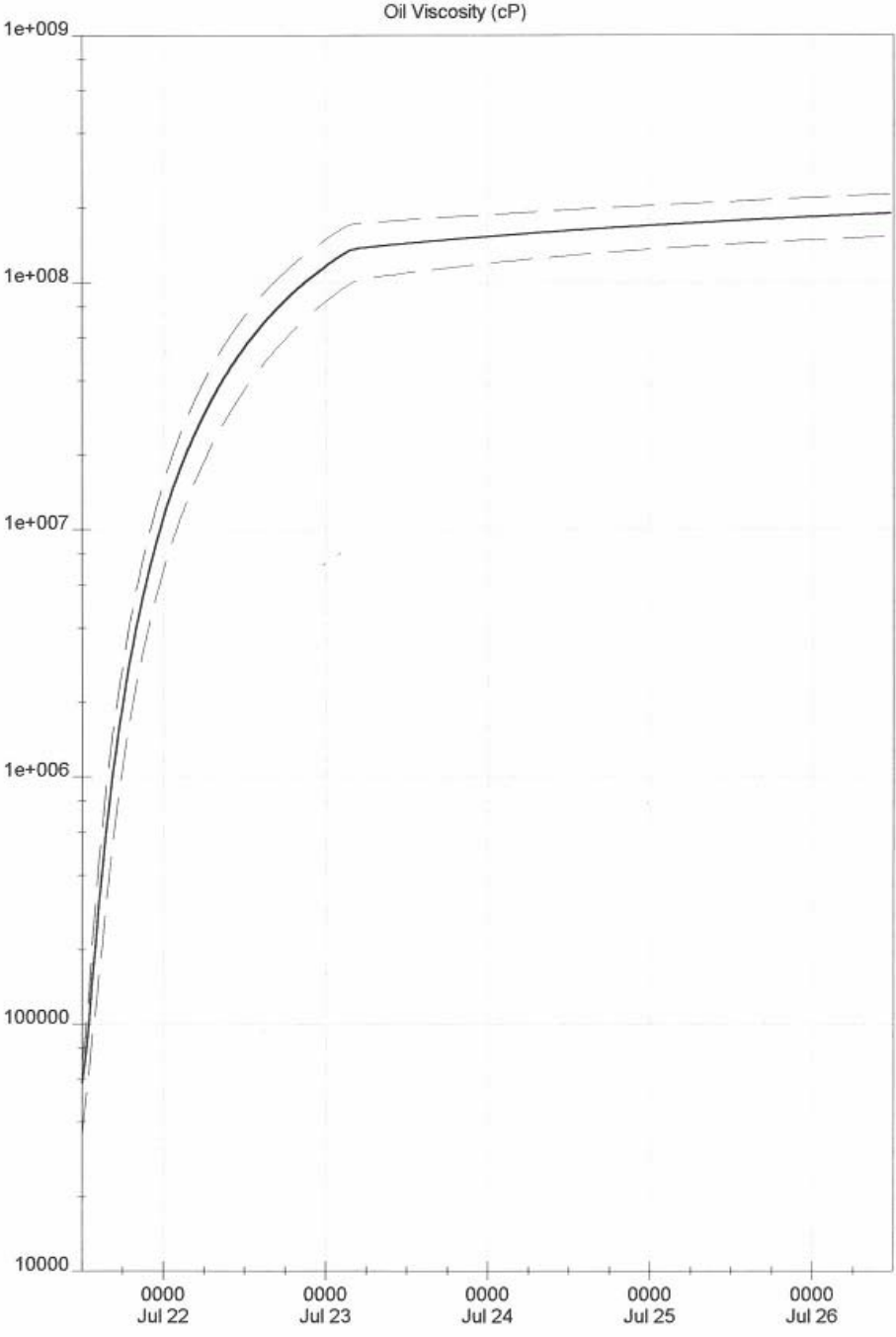
ADIOS® 2.0 



July 21, 2005

Spill Scenario

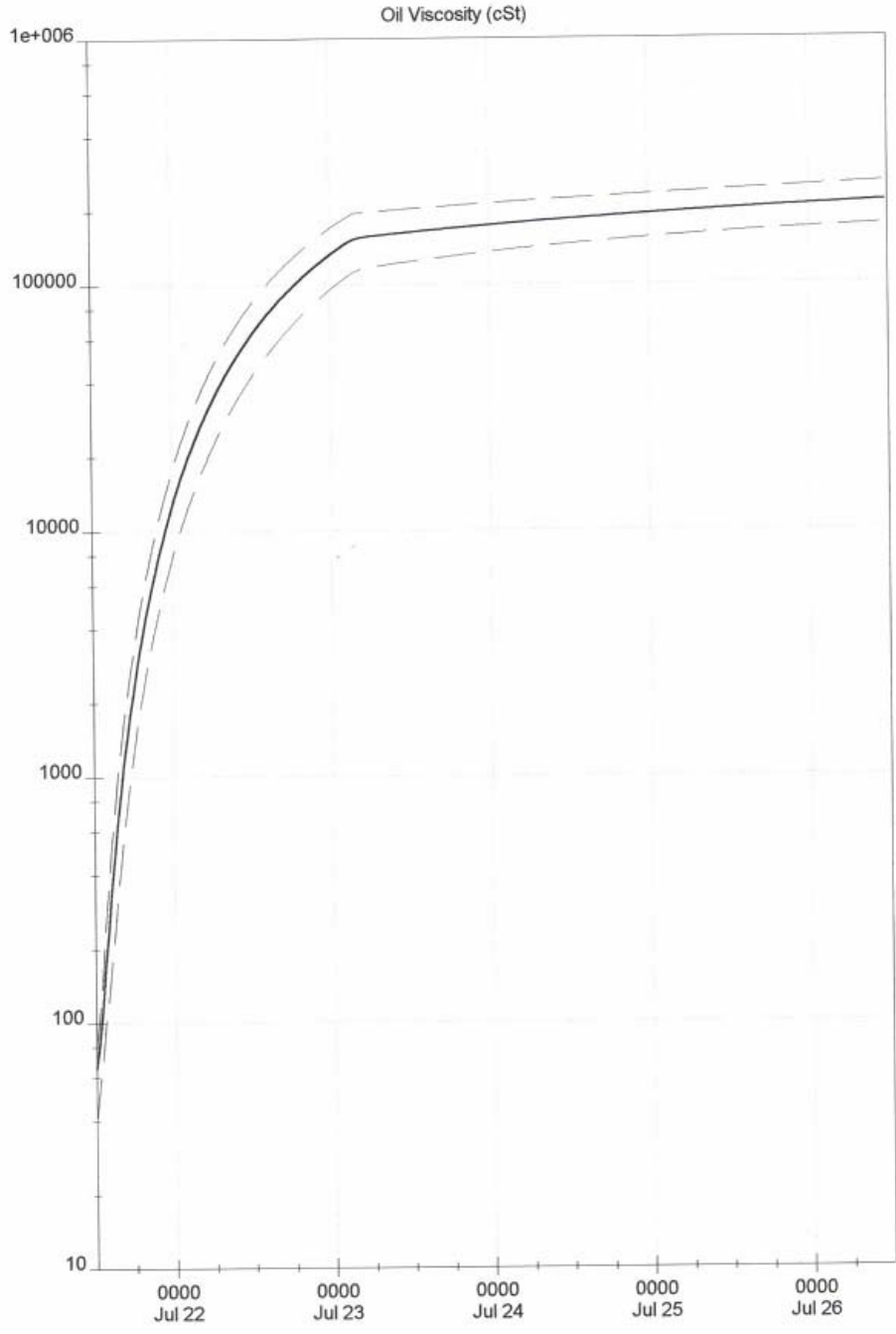
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July 21, 2005

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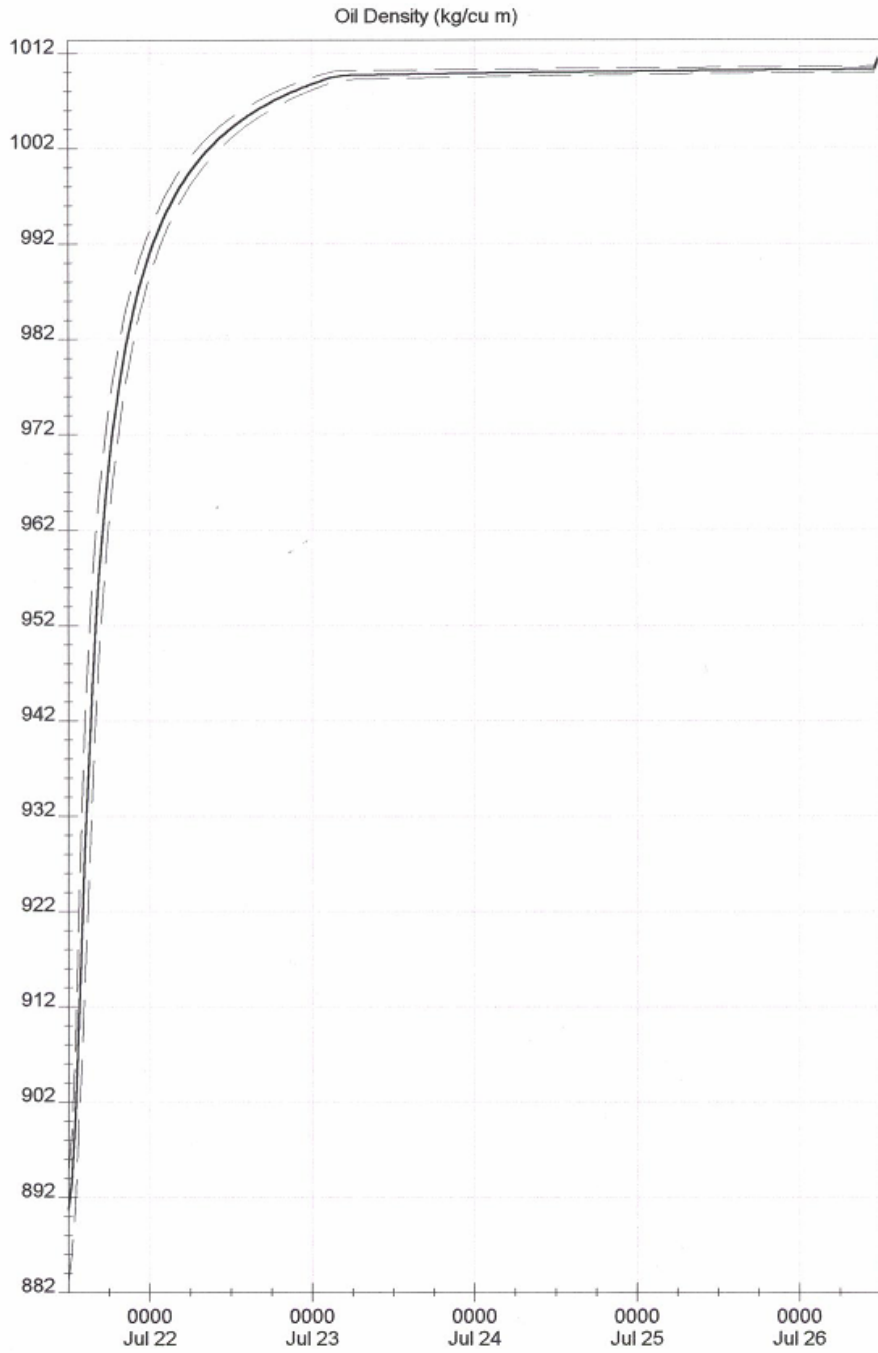
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July 21, 2005

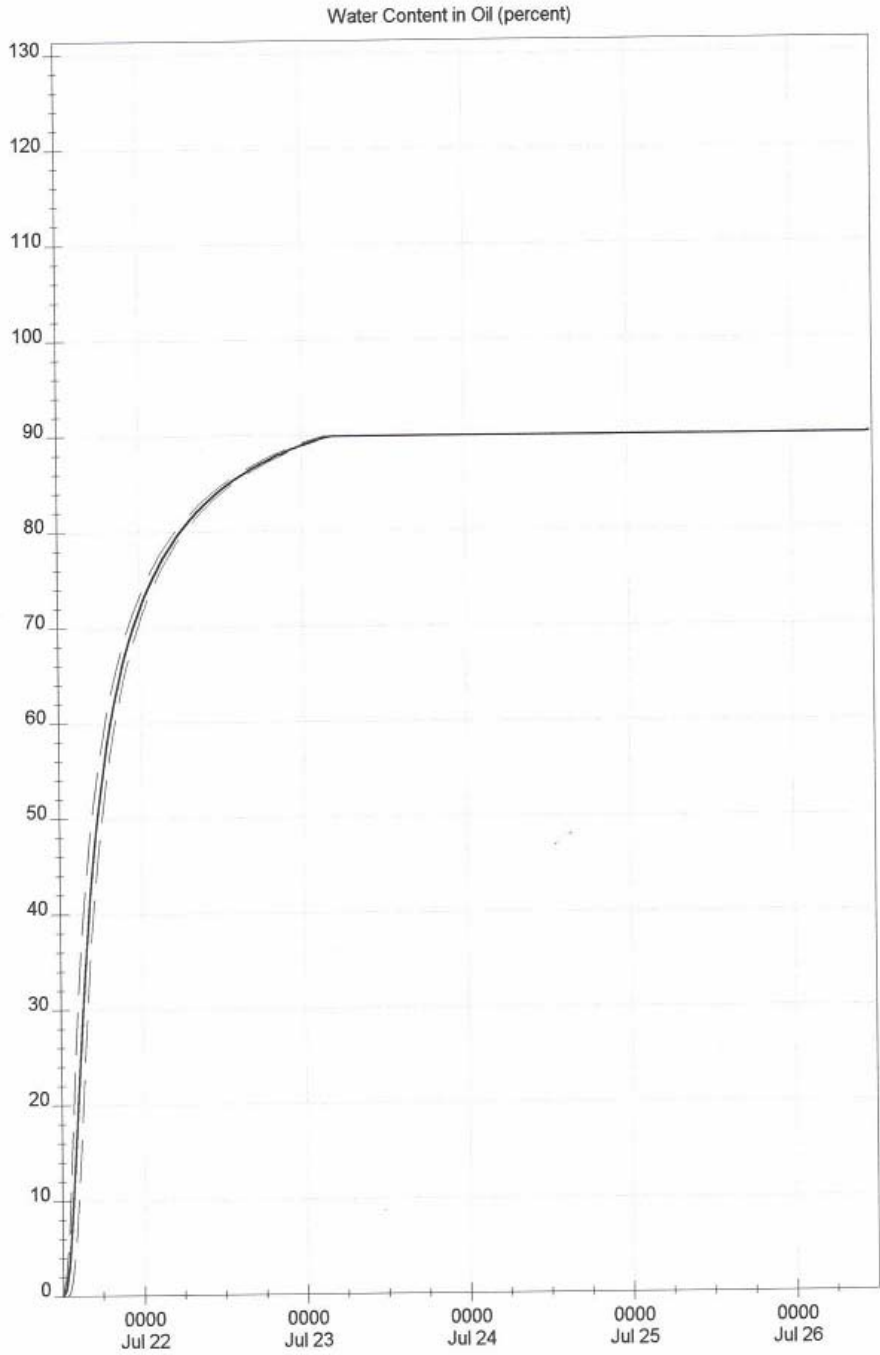
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ADIOS® 2.0



July 21, 2005

Spill Scenario



July 21, 2005

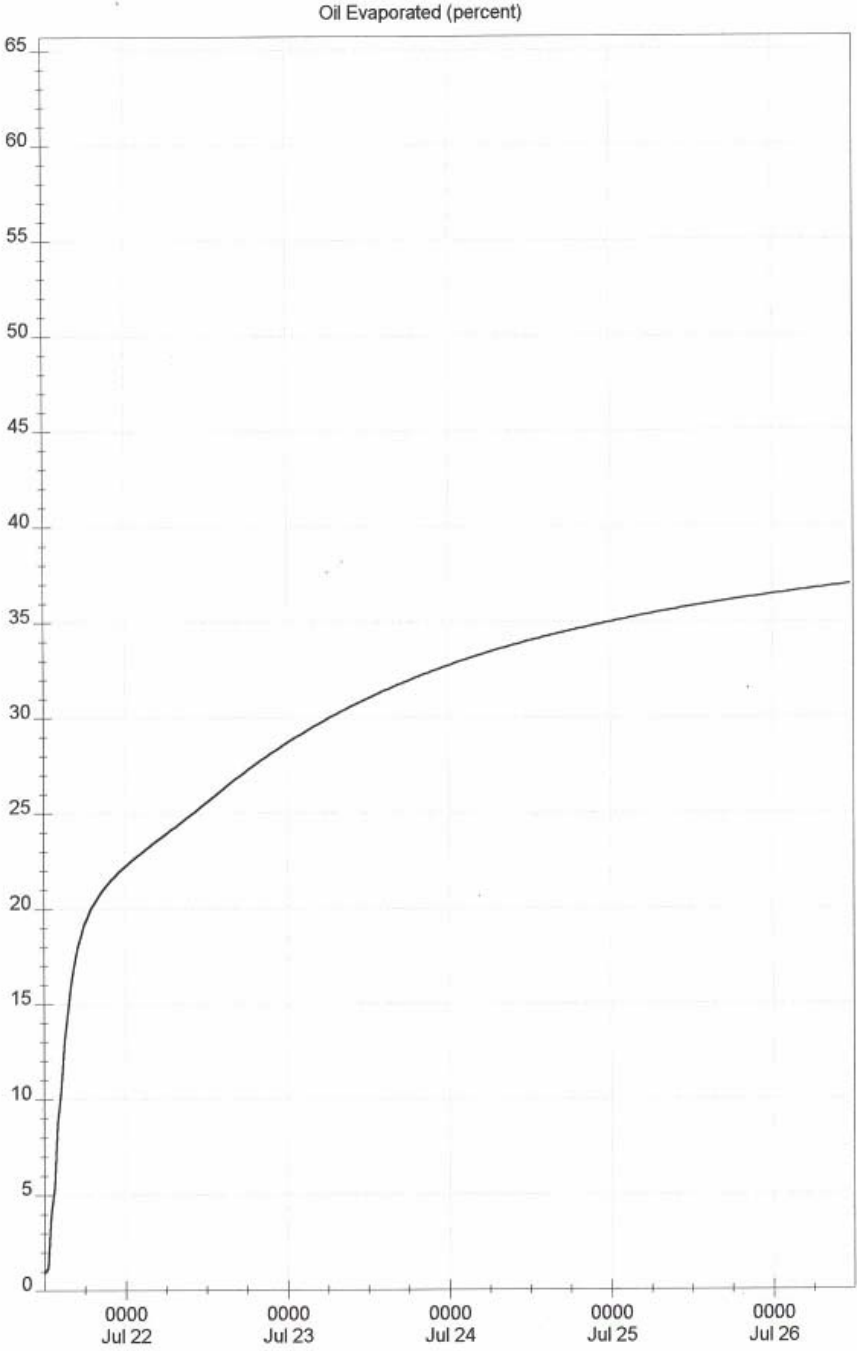
APPENDIX B**ADIOS MODEL – KUWAIT CRUDE OIL****Spill Scenario**

ADIOS® 2.0

**• Oil Type****KUWAIT EXPORT****Location = KUWAIT****Synonyms = none listed****Product Type = crude****API = 31.4****Pour Point = -15 deg C****Flash Point = unknown****Viscosity = 58.1 cP at 38 deg C****Adhesion = unknown****Aromatics = unknown****• Wind and Wave Conditions****Wind Speed = 13 mph from 55 degrees****• Water Properties****Temperature = 60 deg F****Salinity = 27 ppt****Sediment Load = 5 g/m³ (ocean)****Current = 0 mph****• Release Information****• Instantaneous Release****Time of Release = July 21, 1200 hours****Amount Spilled = 10000 bbl**

Spill Scenario

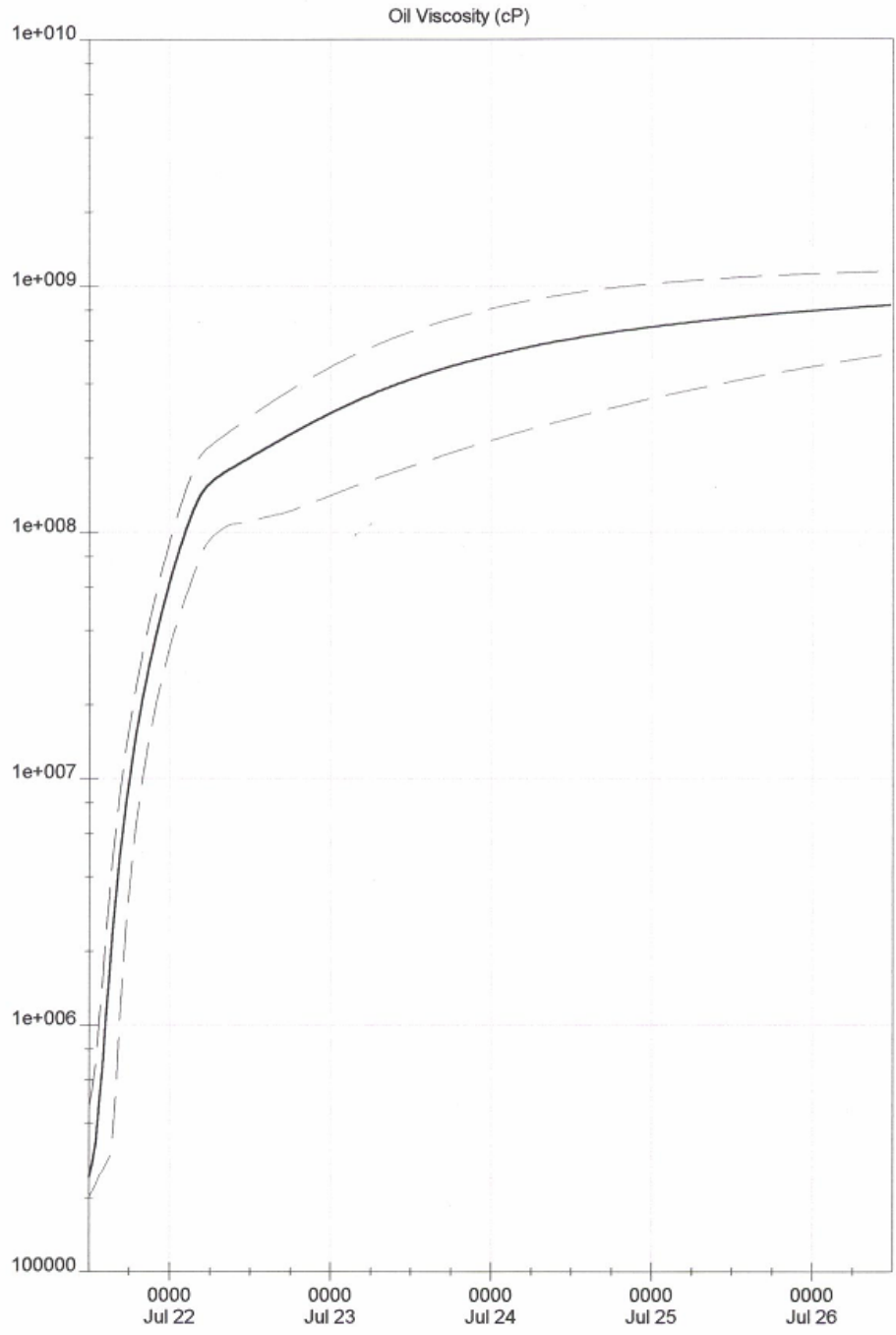
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July 21, 2005

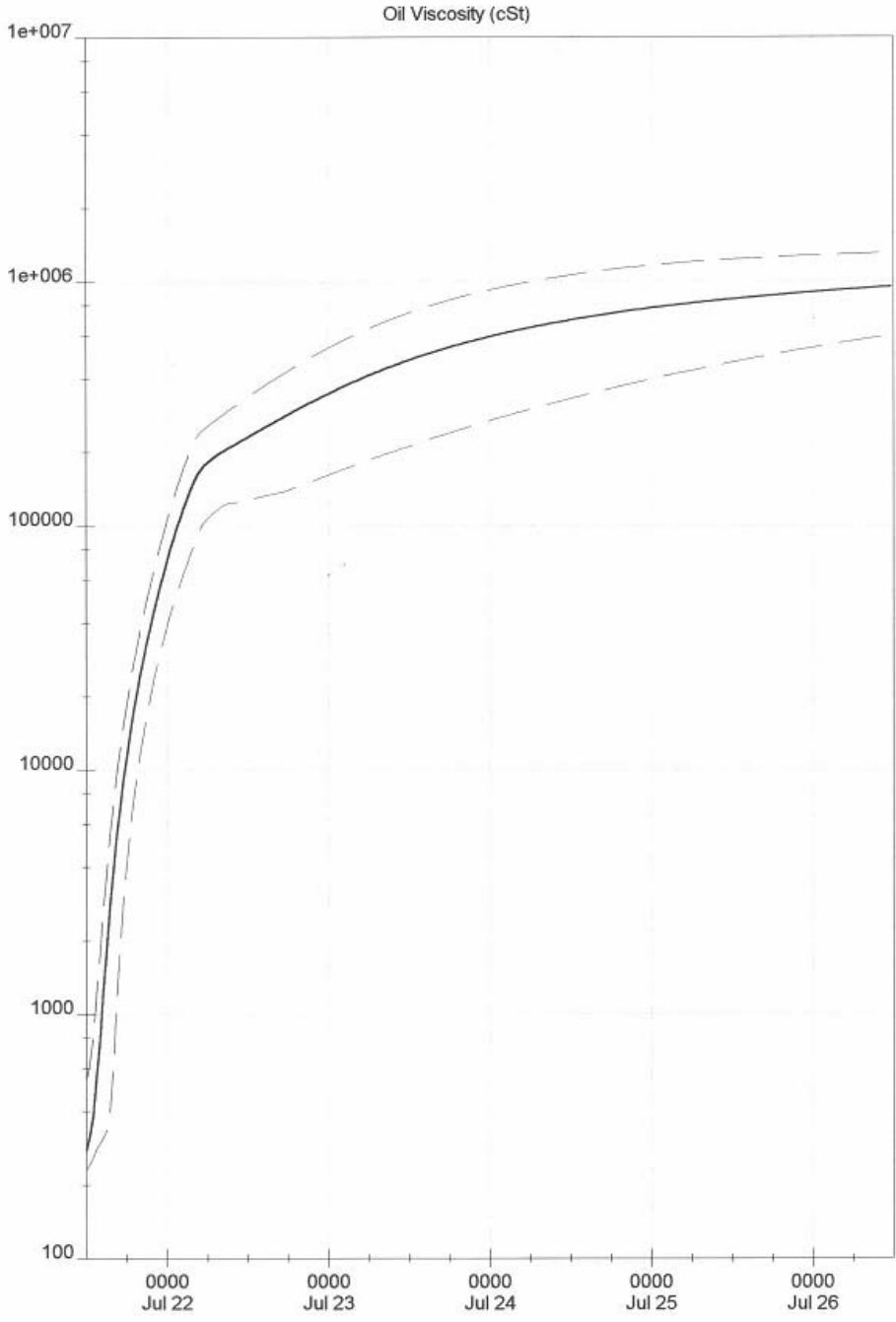
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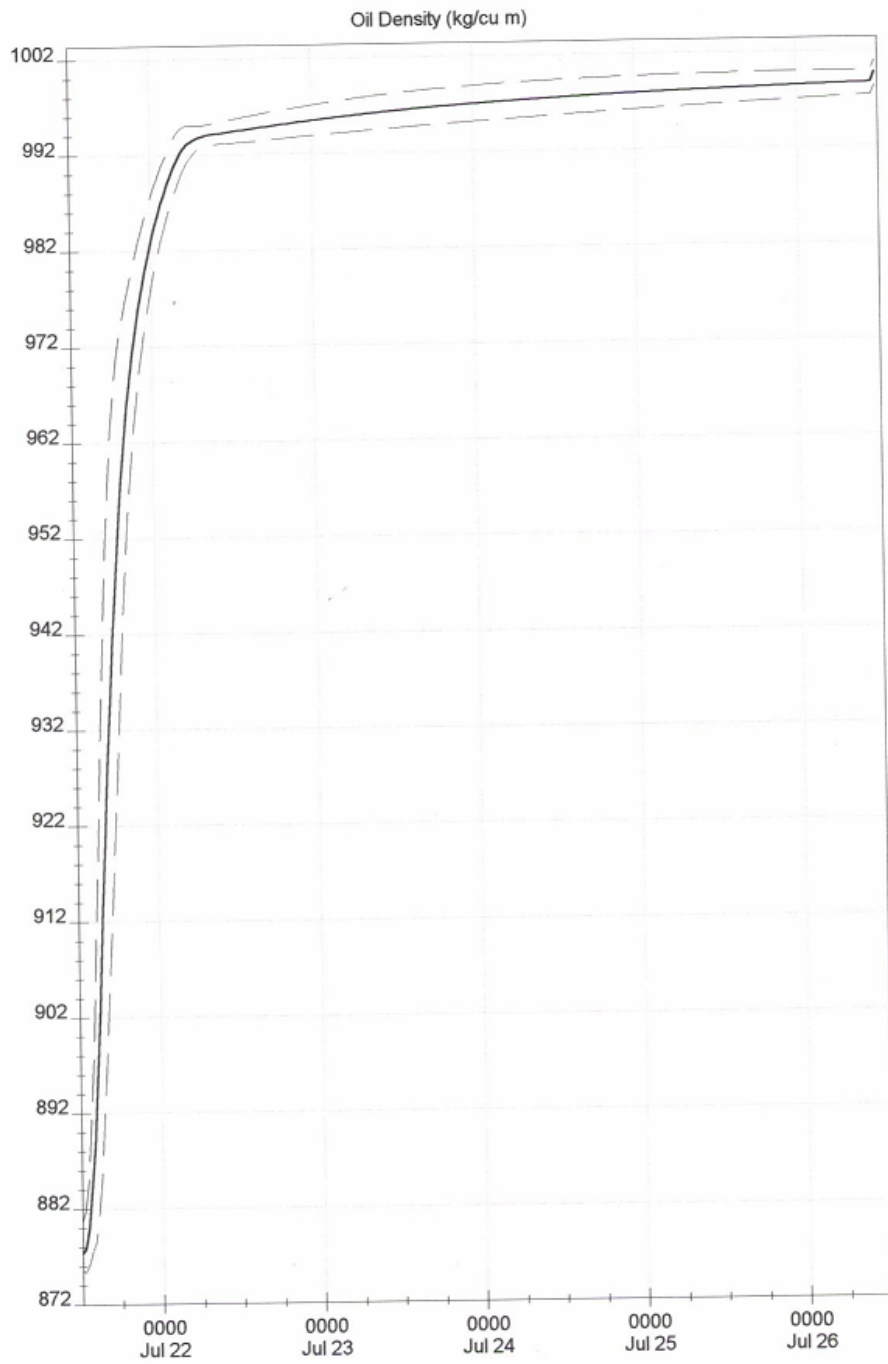
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July 21, 2005

Spill Scenario

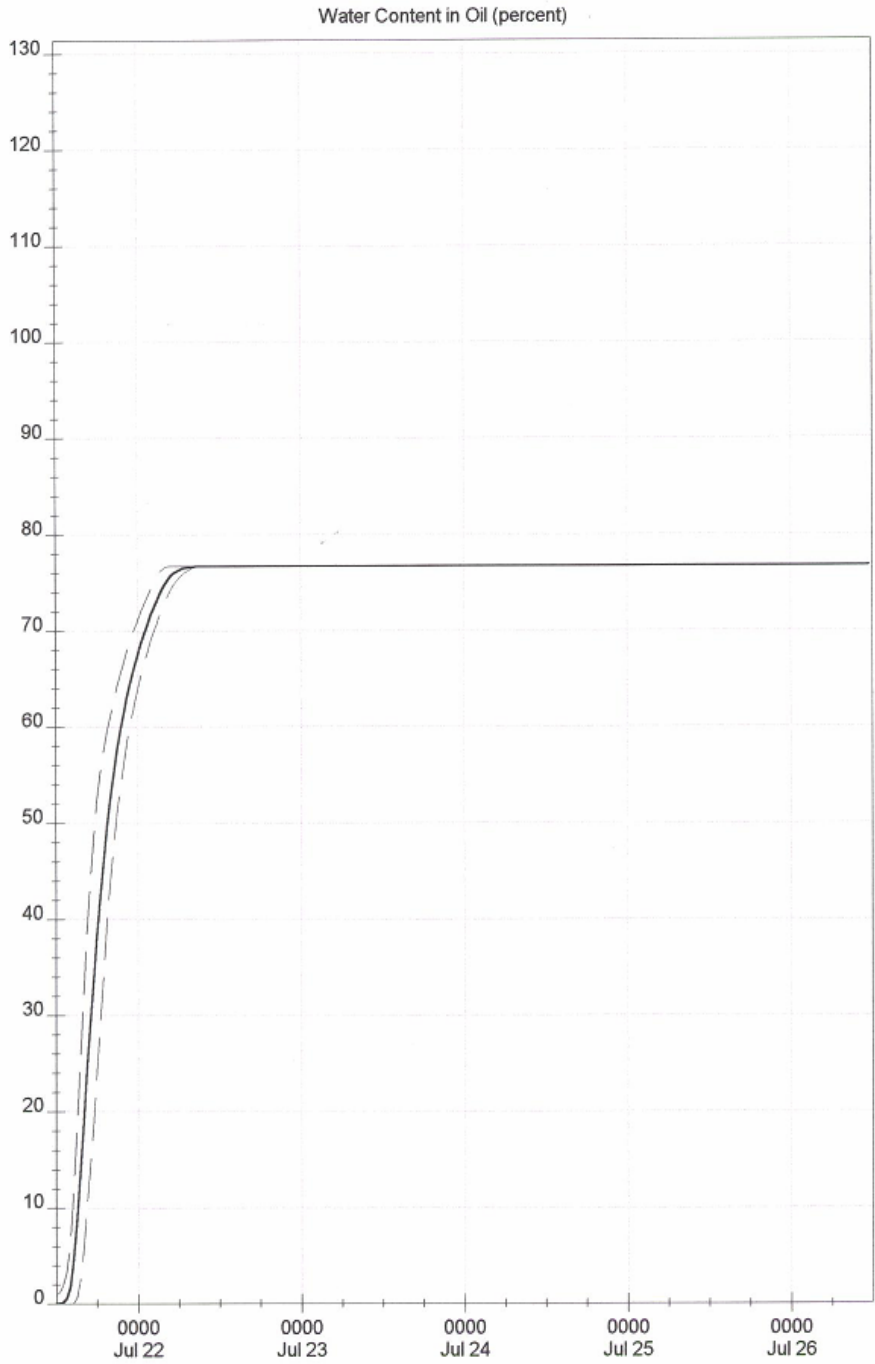
ADIOS® 2.0



July 21, 2005

Spill Scenario

ADIOS® 2.0 



July 21, 2005

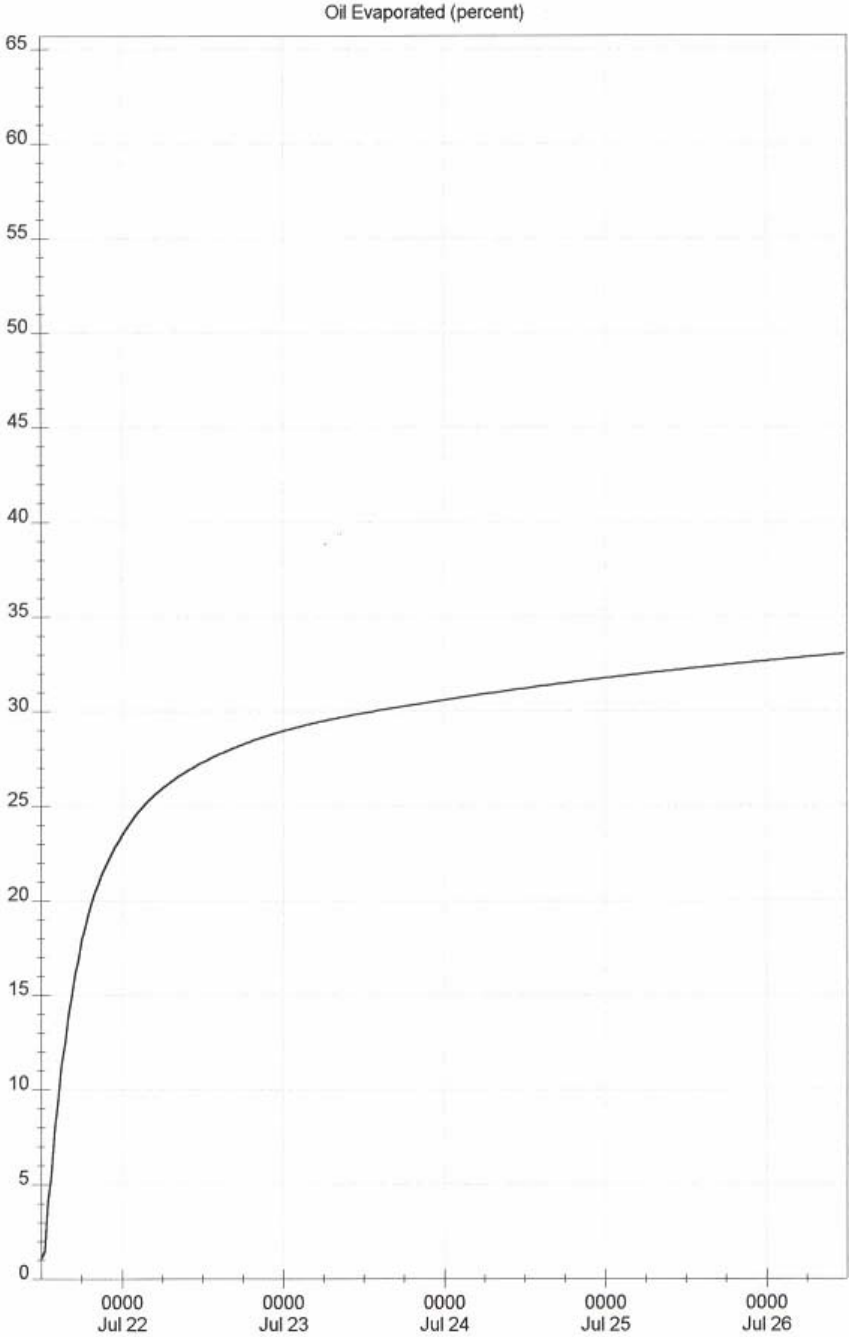
APPENDIX C**ADIOS MODEL – LOUISIANA CRUDE OIL****Spill Scenario**

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**• Oil Type****LOUISIANA****Location = LOUISIANA, USA****Synonyms = none listed****Product Type = crude****API = 34.5****Pour Point = -28 deg C****Flash Point = -11 deg C****Density = 0.863 g/cc at 0 deg C****Viscosity = 15.0 cP at 0 deg C****Adhesion = 0.18g/m²****Aromatics = 21 weight %****• Wind and Wave Conditions****Wind Speed = 13 mph from 55 degrees****• Water Properties****Temperature = 60 deg F****Salinity = 27 ppt****Sediment Load = 5 g/m³ (ocean)****Current = 0 mph****• Release Information****· Instantaneous Release****Time of Release = July 21, 1200 hours****Amount Spilled = 10000 bbl**

Spill Scenario

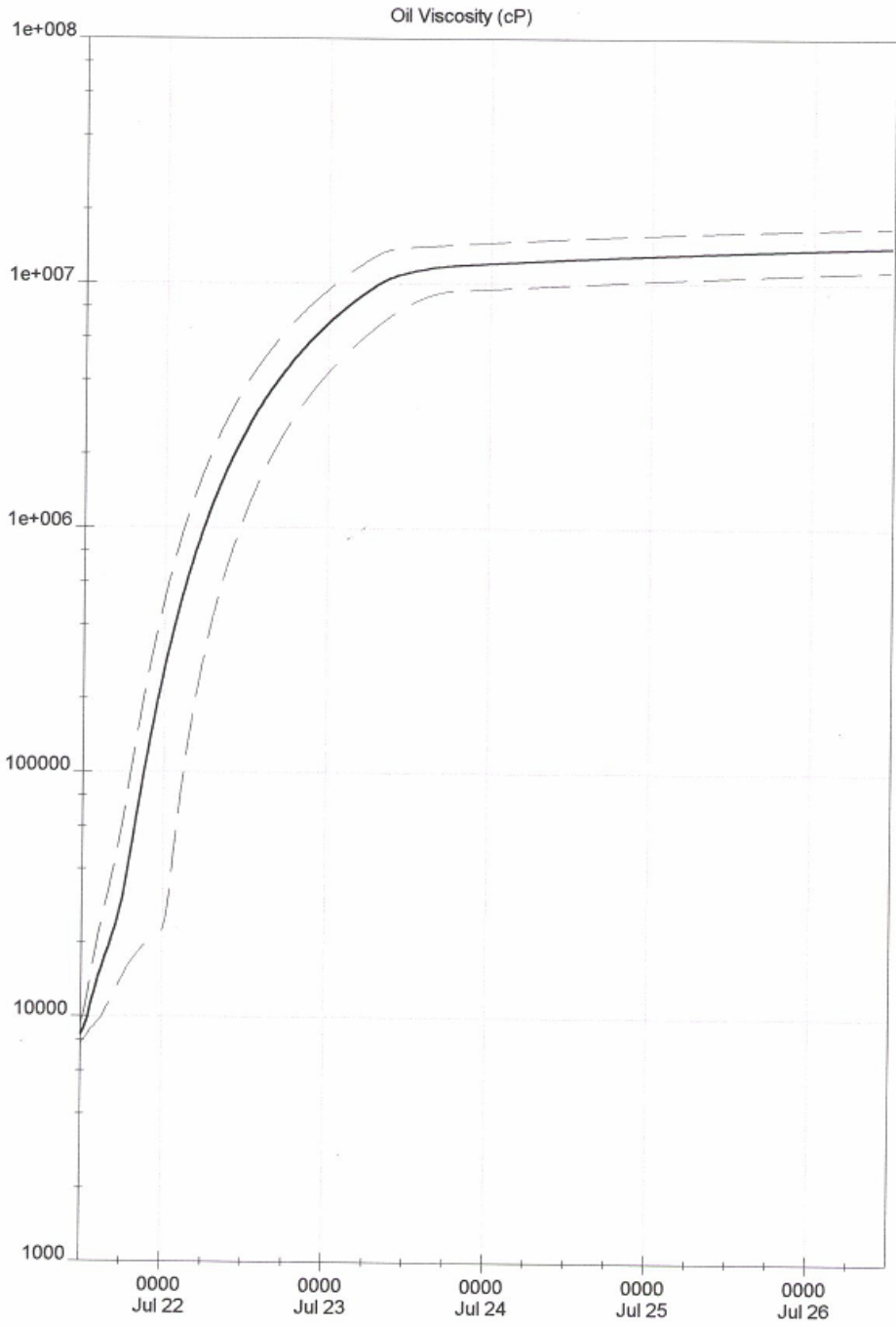
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Spill Scenario

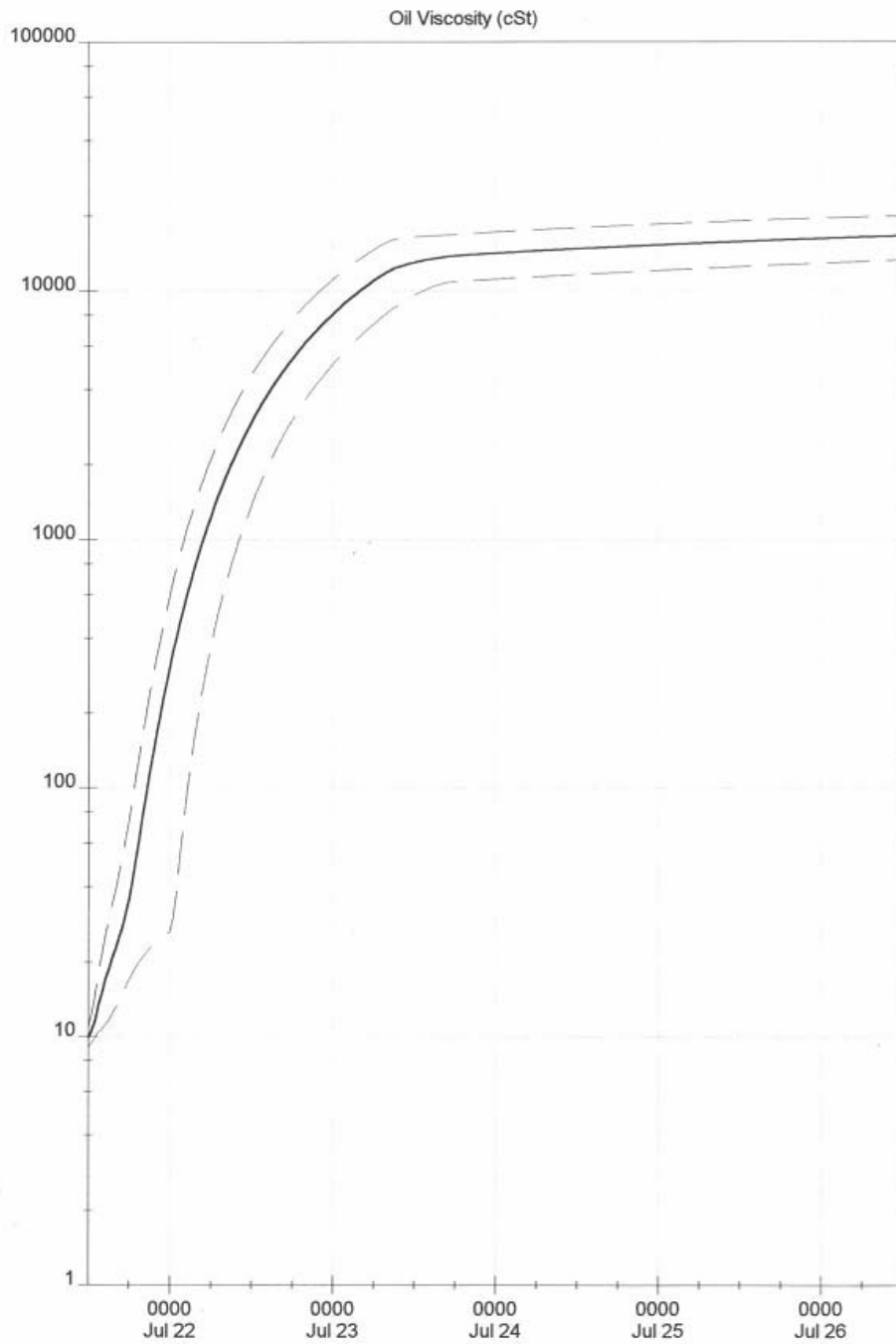
ADIOS® 2.0 



July 21, 2005

Spill Scenario

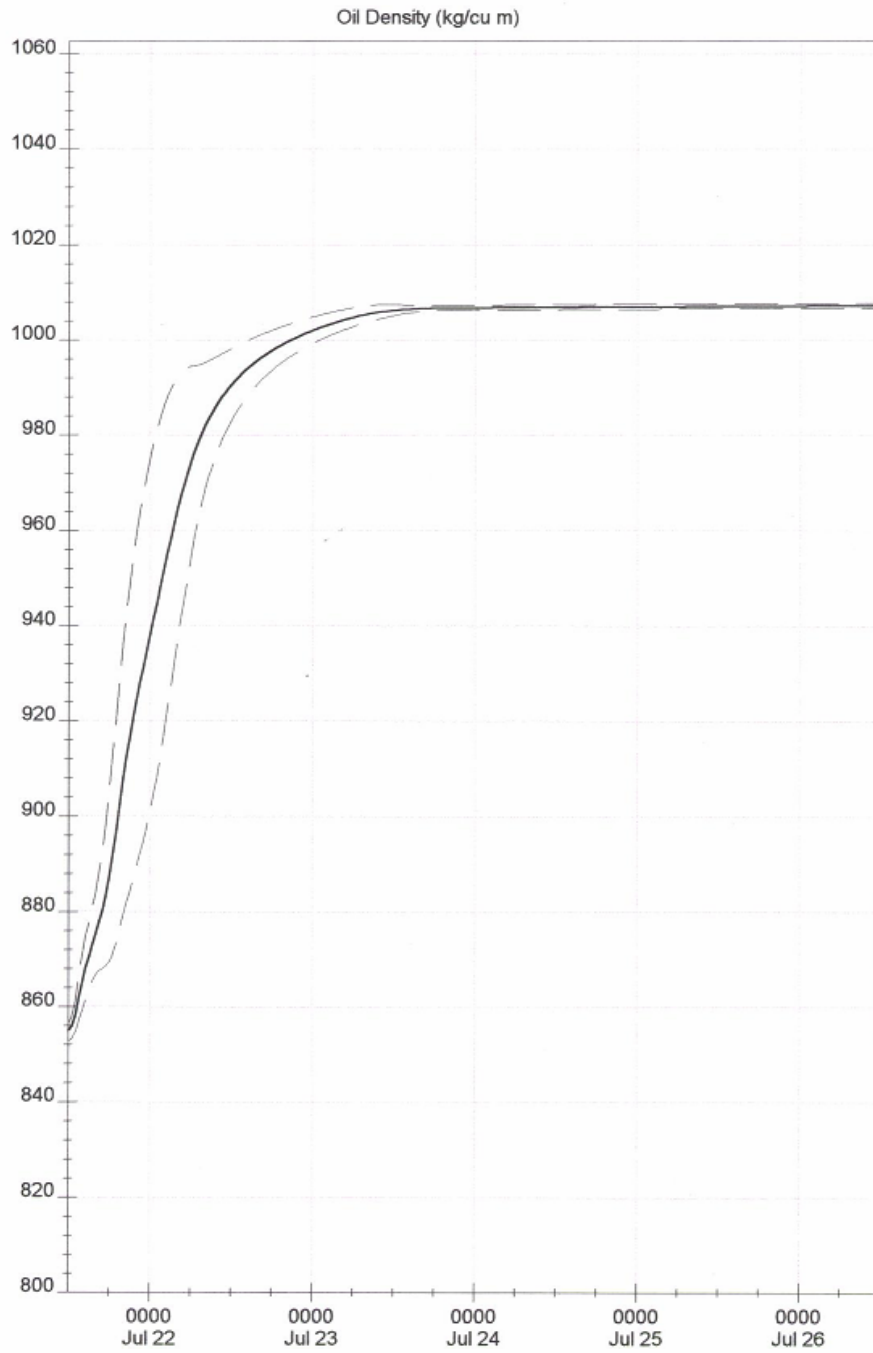
ADIOS® 2.0



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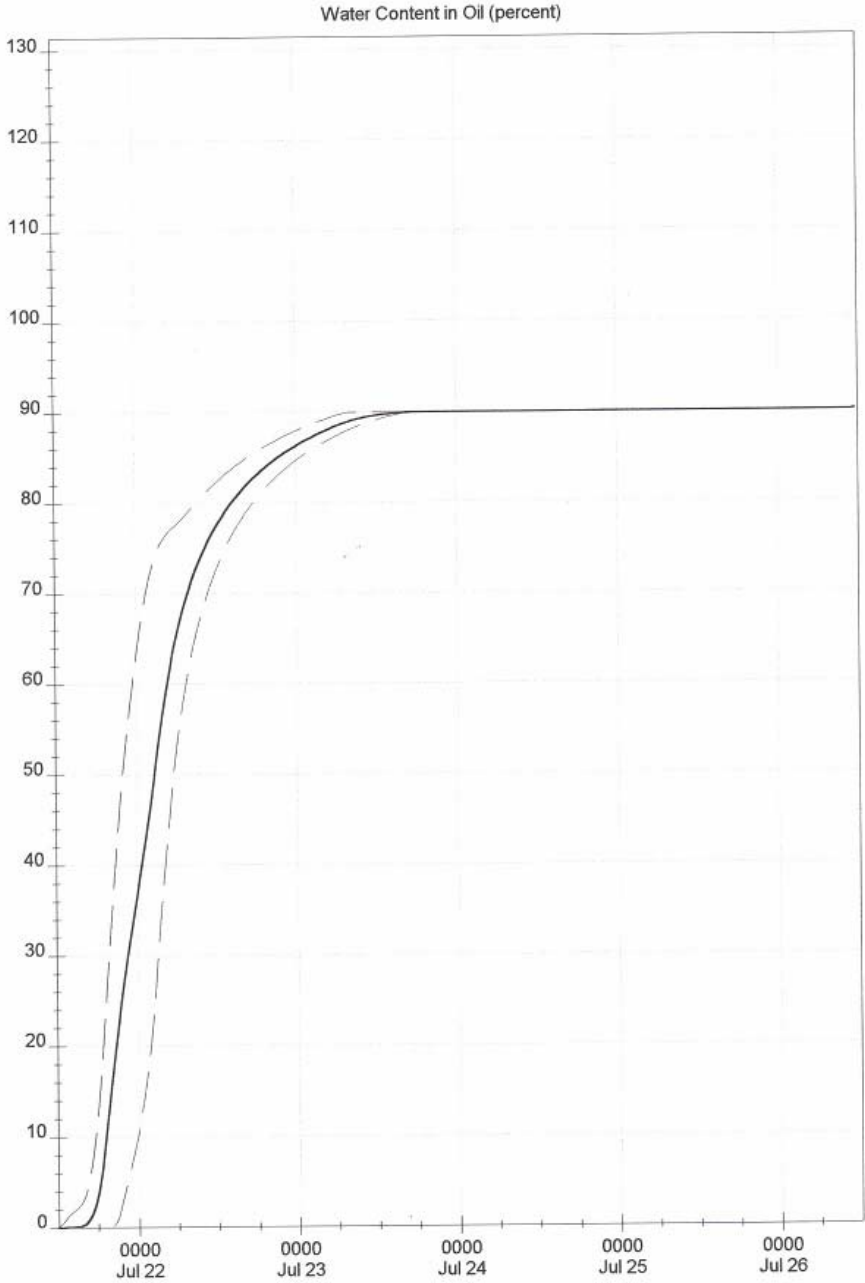
Spill Scenario

ADIOS® 2.0



July 21, 2005

Spill Scenario



July 21, 2005

APPENDIX D

ADIOS – ADDITIONAL OUTPUT

Evaporation: The graph shows the amount of crude oil lost due to evaporation. ADIOS will normally predict for 5 days unless there is insufficient wind data.

In the graph, the solid line shows the best estimate.

Viscosity: The graph shows the change in the crude oil emulsion viscosity as the slick weathers. ADIOS normally predicts for 5 days, unless there is insufficient data.

In the graph, the solid line shows the average value and the grey area shows the expected range in values throughout the slick.

There can be a large change in the viscosity, as slick weathers, particularly if the oil emulsifies. Hence, ADIOS viscosity predictions are plotted using logarithmic vertical scale.

Density: This graph shows the change in the crude oil emulsion density as the slick weathers. ADIOS will normally predict for 5 days unless there is insufficient wind data.

In the graph, the solid line shows the average value and the gray area shows the expected range in values throughout the slick.

In general, density changes for weathered crude oil are small and the oil, if initially buoyant, will remain buoyant.

The ADIOS weathering algorithm will not cause a floating crude oil to become more dense than surrounding water

Water Content Graph: This graph shows the water percent fraction of the emulsified crude oil. ADIOS will normally predict for 5 days unless there is insufficient wind data.

In the graph, the solid line shows the average value and the gray area shows the expected range in values throughout slick. The refined products will not emulsify.

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