BITUMENS AND DILUTED BITUMENS FROM WESTERN CANADIAN OIL SANDS

An article on Bitumens and Diluted Bitumens from Western Canadian Oil Sands contributed by Dr Merv Fingas of Spill Science, Edmonton, Alberta, Canada. fingasmerv@shaw.ca

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Bitumens and Diluted Bitumens from Western Canadian Oil Sands

This serial will cover the topic of bitumen products such as from the Canadian Oil Sands and diluted bitumen products (Dilbit and others). This is the first of nine issues by Dr. Merv Fingas, ISCO member for Canada.

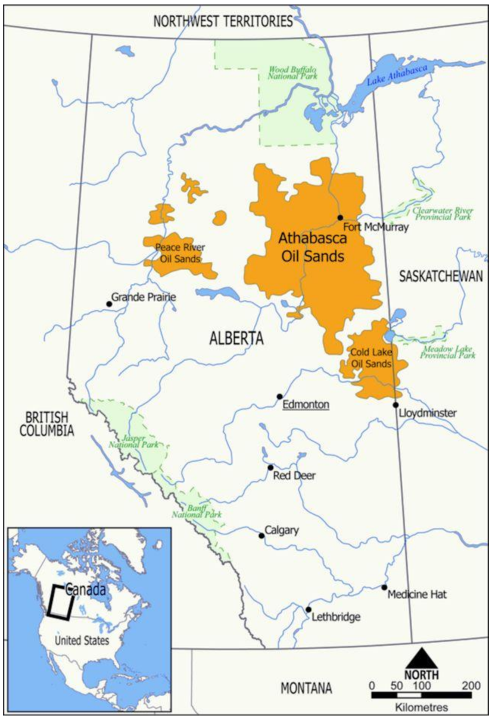
Summary

This series is a summary of several physical parameters and the spill behavior of diluted bitumens and other bitumen products. There are three basic types of diluted bitumen based on the diluents used to lower the bitumen viscosity. The most typical type is diluted with various condensates and these are called Dilbits, alternatively there are some diluted with naphtha. A newer type that is emerging is diluted with C4 or a butanes mixture (sometimes including C5 or a pentanes mixture), often along with condensates. Synthetic crude is sometimes used as a diluent and this type is called Synbit. Other variants on these include Railbit, similar to Dilbit but diluted half as much and Neatbit, which is not diluted at all. Each of these bitumen products has different properties initially when spilled, however with time, generally revert to the properties of the starting bitumen except for Synbit which tends to weather much less. The properties of the starting bitumens vary widely, as do the diluents, resulting in highly variable products with highly variable behaviors.

Definitions

Bitumen – heavy oil from oil sands
Condensate – a light oil product typically produced from a gas well and used as a diluent for transporting bitumen products
Dilbit – diluted bitumen with about 30% diluent, typically transported by pipeline
Dilsynbit – diluted bitumen with synthetic crude and another diluent – usually condensate
Diluent – traditionally condensate but could be a variety of materials
Neatbit – undiluted bitumen, if shipped, would be shipped by heated rail tank cars
Railbit – diluted bitumen with about 15% diluent, typically shipped by rail tank car
Synbit – bitumen diluted with synthetic crude
Dilsynbit – diluted bitumen with synthetic crude and another diluent – usually condensate

1.1 Introduction



This series deals with products deriving from Canada's oil sands, the majority of which are located in Alberta. Figure 1 shows the location of these oil sands.

Figure 1 *Location of the three major Oil Sands deposits*

These oil sands cover over an area about twice the area of Florida and are the third largest oil deposit in the world.

The Alberta oil sands have been produced for about 40 years. More than 25 companies now producing at more than 7 sites – about 3 new sites added per year (about $ 50 billion construction projects are underway now).

There is variance in production methods and in refining methods, therefore the bitumen produced is highly variable in properties. Bitumen is typically marketed as a refined product (Synthetic crude) or as a diluted product (Dilbit).

1.2 Background

The objective of this paper is to provide countermeasures and environmental prediction information on the three types of diluted bitumen.

Because of the high variability of each of the products, there is a high variability in behavior; this becomes very important to dealing with the products once spilled.

Diluted bitumens can be divided into four classes dependent on the diluent:

- Standard Dilbit, if the diluent is a gas condensate,
- Synbit, if the diluent is a synthetic crude,
- Lightened Dilbit, if the diluent is a gas condensate with added C4 and/or C5 diluents, herein called C4/C5 enhanced Dilbit, or
- Dilbit diluted with a synthetic naphtha.

Synbits are sometimes modified by the addition of a gas condensate to meet pipeline specifications and these are alternatively called Dilsynbits.

The dilution of bitumen is governed by pipeline specifications which are in turn governed by pumping and pipe considerations. The most common specification for pipeline inputs is a maximum of 940 kg/m3 (0.94 g/mL) density and 350 cSt (mPa.s) viscosity (NRC, 2013).

1.3 A Summary of Oil Composition and Behavior

Petroleum oils, including bitumens, are mixtures of hydrocarbon compounds ranging from smaller, volatile compounds to very large, non-volatile compounds (ESTC, 2014; AOSTA, 1984; NRC, 2013). This mixture of compounds varies according to the geological formation of the area in which the oil is found and strongly influences the properties of the oil. Petroleum products such as gasoline or diesel fuel are mixtures of fewer compounds and thus their properties are more specific and less variable. Hydrocarbon compounds are composed of hydrogen and carbon, which are therefore the main elements in oils. Oils also contain varying amounts of sulphur, nitrogen, oxygen, and sometimes mineral salts, as well as trace metals such as nickel, vanadium, and chromium. One thing that must be stressed about petroleum, especially crude oils and bitumens, is that they are highly varied products in terms of composition. Composition varies extensively between batches and times of production. This results in a corresponding variability in properties and behavior.

In general, the hydrocarbons found in oils are characterized by their structure. The hydrocarbon structures found in oil are saturates, aromatics, and polar compounds. The saturate group of components in oils consists primarily of alkanes, which are compounds of hydrogen and carbon with the maximum number of hydrogen atoms around each carbon. Thus, the term 'saturate' is used because the carbons are 'saturated' with hydrogen. Larger saturate compounds are often referred to as 'waxes'. The aromatic compounds include at least one benzene ring of six carbons. Three double carbon-to-carbon bonds float around the ring and add stability. Because of this stability, benzene rings are very persistent and can have toxic effects on the environment.

The most common smaller and more volatile compounds found in oil are often referred to as BTEX, or benzene, toluene, ethyl-benzene, and xylenes. Polyaromatic hydrocarbons or PAHs are compounds consisting of at least two benzene rings.

Polar compounds are those that have a significant molecular charge as a result of bonding with compounds such as sulphur, nitrogen, or oxygen. The 'polarity' or charge that the molecule carries results in behavior that may be different from that of un-polarized compounds. In the petroleum industry, the smallest polar compounds are called 'resins', which are largely responsible for oil adhesion. The larger polar compounds are called 'asphaltenes' and they often make up the largest percentage of the asphalt commonly used for road construction. Asphaltenes often consist of very large molecules and, if in abundance in an oil, they have a significant effect on oil behavior. Bitumen contains significant but varying amounts of asphaltenes.

References:

AOSTA, The Thermodynamic and Transport Properties of Heavy Oils and Bitumen, AOSTA - Alberta Oil Sands Authority, 1984
ESTC (Environmental Technology Centre), World Catalogue of Oil Properties, WWW.ETC-CTE.ec.gc.ca, 2014.

NRC, TRB Special Report 311: Effects of Diluted Bitumen on Crude Oil Transmission Pipelines, The National Academies Press, Washington, DC, 2013

1.3.1 Bitumen

The composition of the oil sands and related bitumens are dominated by unresolvable compounds.

These oils, however, can be refined into usable products. To be transported to refineries, bitumens must be diluted with condensates or with synthetic crude oils.

The properties of some bitumens are given in Table 1 (ESTC, 2014).

Table 1 Bitumen Properties

(ETC - 2014, AOSTA, 1984)

Name	Density Range	Viscosity Range	Sulphur %
	kg/m^3	mPa.s (cSt)	%
Athabasca	1006 to 1016	90,000 to 900,000	4.4 to 5.4
Cold Lake	977 to 1006	100,000 to 450,000	4.1 to 6.9
Lloydminster	980 to 1016	100,000 to 450,000	4.1 to 6.9
Peace River	1001 to 1006	90,000 to 900,000	4.4 to 5.4

1.3.2 Condensates

Condensates are liquid hydrocarbons taken from gas wells and gas production facilities.

These condensates vary widely, however in Alberta there are several steady streams which are used as bitumen diluents as shown in Table 2 (Crude Monitor, 2014).

Table 2 Condensates

(Crude Monitor, 2014)

Name	Supplier	Density	Sulphur %	BTEX total
		kg/m^3	(%)	(vol %)
CRW (blend)	Enbridge Aggregate	715	0.15	3.92
Fort Saskatchewan Condensate	Keyera	679	0.04	2.51
Peace Condensate		751	0.21	5.02
Pembina Condensate	Pembina pipeline	758	0.11	5.92
Rangeland Condensate	Plains Midstream	757	0.25	5.35
Southern Lights Diluent	U.S. Midwest	674	0.02	2.6

Enbridge uses significant amounts of condensate to transport Dilbit in pipelines.

Enbridge has set minimum specifications for this diluent condensate as shown in Table 3 (CAPP, 2012).

Table 3 Specifications for condensates

(Crude Monitor, 2014)

Quality parameter	**Units**	**Minimum**	**Maximum**
Density	kg/M^3	600	775
Viscosity	cSt		2
Sulphur total	wt%		0.5
Olefins	wt%		<1
Reid Vapor Pressure	kPa		103
Aromatics (BTEX)	vol%		2
Mercaptans & volatiles <C3	ppm		175
H_2S	ppm		20
Benzene	vol %		1.6
Mercury	wppb		10
Oxygenates	m		100
Filterable solids	mg/L		200

1.3.3 Diluted Products

1.3.3.1 Dilbits

Dilbit, the mixture of two highly variable products, bitumen and diluent, results in very variable end products.

Table 4 shows the summary properties of various Dilbits (Crude Monitor, 2014). It should be noted that these properties are similar if the diluent is straight condensate or a C4/C5 enhanced condensate.

Table 4 Dilbits
(viscosity < 300 cSt or mPa.s)

(Crude Monitor, 2014)

Name	**Diluent**	**Density**	**Sulphur %**
		kg/m^3	**(%)**
Access Western Blend (AWB)		923	3.9
Borealis Heavy Blend (BHB)	hydro-treated naphtha	926	3.8
Christina Dilbit Blend		924	3.9
Cold Lake Dilbit	condensate	928	3.8
Kearl Lake Dilbit		927	3.8
Peace River Heavy crude		928	5.1
Statoil Cheecham Blend		929	3.8
Western Canadian Select (WCS)		929	3.5

A comment on the use of C4/C5 to supplement condensate as a diluent, should be added here. There is shortage of condensate in Western Canada to dilute bitumen (Armstrong and Brandt, 2013; KMC, 2013). This shortage will continue to rise in the future, necessitating the use of other products to dilute bitumen.

One of the solutions at this time is to use C4 (butanes) and C5 (pentanes) as a supplement to the diluent streams to extend the amount of condensate needed. This reduces the amount of condensate needed to meet pipeline minimum specifications, however increases the flammability of the product when released and decreases the Dilbit stability.

An increasing amount of alkanes such as C4 or C5 can cause the asphaltenes to precipitate which could cause great difficulty for a pipeline.

Currently, the amount of C4 is set to a maximum of 5% (of total oil mass) after which there is a penalty for this product. The resulting properties of the Dilbits shown in Table 4 would not change much with the addition of C4, however less diluent would be used.

1.3.3.2 Synbits

Synbits are almost as variable in properties as Dilbits, however, in terms of oil spill countermeasures are quite different. The end properties after weathering are much less viscous and dense than those of Dilbits. The diluent used in a Synbit is a synthetic crude oil, namely a crude oil made by initial refining of bitumen.

The properties of the synthetic crudes are much closer to those of the bitumen and thus there is not as much of a change in properties after release. Properties of some Synbits are shown in Table 5 (Crude Monitor, 2014).

Table 5 Synbits

(viscosity < 300 cSt or mPa.s) (Crude Monitor, 2014)

Name	**Source**	**Density**	**Sulphur %**
		kg/m^3	**(%)**
Long Lake Heavy crude	North East AB	929	3
Mackay River crude	North East AB	936	2.8
Statoil Cheecham Synbit	North East AB	931	3.1
Suncor Synthetic	North East AB	927	3.1
Surmont Heavy Blend	North East AB	936	3
Albian Heavy Synthetic crude*	Edmonton area	926	2.4

* also shipped as a DilSynBit

A variation on the theme of a Synbit is the product known as a Dilsynbit, which is a Synbit additionally diluted with condensate to allow the product to meet pipeline specifications.

References:

AOSTA, *The Thermodynamic and Transport Properties of Heavy Oils and Bitumen*, AOSTA - Alberta Oil Sands Authority, 1984

Armstrong, M., and M. Brandt, *Strategies for Improved Naphtha Processing*, http://www.digitalrefining.com/article_1000881.pdf, 2013

CAPP, Quality Guidelines for Western Canadian Condensate, Presentation by Randy Segato, Suncor, to CAPP, 2012.

Crude Monitor, http://www.crudemonitor.ca/home.php, 2014

ESTC (Environmental Technology Centre), *World Catalogue of Oil Properties*, WWW.ETC-CTE.ec.gc.ca, 2014.

KMC, *The Diluent Market*, Kinder Morgan Presentation at the Wells Fargo Fundamental Forum, 2013.

1.3.4 Oil and Petroleum Product Properties

The properties of oil discussed here are viscosity, density, specific gravity, solubility, flash point, pour point, distillation fractions, interfacial tension, and vapour pressure.

Viscosity is the resistance to flow in a liquid (Fingas, 2012). The lower the viscosity, the more readily the liquid flows. For example, water has a low viscosity and flows readily, whereas honey, with a high viscosity, flows poorly. The viscosity of the oil is largely determined by the amount of lighter and heavier fractions that it contains. The greater the percentage of light components such as saturates and the lesser the amount of asphaltenes, the lower the viscosity.

As with other physical properties, viscosity is affected by temperature, with a lower temperature giving a higher viscosity. For most oils, the viscosity varies as the logarithm of the temperature, which is a very significant variation. Oils that flow readily at high temperatures can become a slow-moving, viscous mass at low temperatures. In terms of oil spill cleanup, viscosity can affect the oil's behavior. Viscous oils do not spread rapidly, do not penetrate soil as readily, and affect the ability of pumps and skimmers to handle the oil. Dilbits and Synbit start out at a viscosity of about 300 mPa.s, which is like that of light syrup. Weathered Dilbits slowly return to the density of the starting bitumen as shown in Figure 2.

Figure 2 A view of weathered Dilbit showing the viscosity increase after about four days of weathering. The viscosity of the product after spilling slowly returns to the properties of the starting bitumen.

Density is the mass (weight) of a given volume of oil and is expressed in grams per cubic centimetre (g/cm^3) or equivalently kilograms per cubic metre (kg/m^3). It is the property used by the petroleum industry to define light or heavy crude oils. Density is also important as it indicates whether a particular oil will float or sink in water. As the density of water is 1.0 g/cm^3 at 15^{o}C and the density of most oils ranges from 0.7 to 0.99 g/cm^3, most oils will float on water. The density of most bitumens range from 0.997 to as high as 1.016. As the density of seawater is 1.03 g/cm^3, even heavier oils will usually float on it. Many bitumens sink in fresh water. As the light fractions evaporate with time, the density of oil increases, such as is the case for Dilbits.

Another measure of density is specific gravity, which is an oil's relative density compared to that of water at 15°C. Another gravity scale is that of the American Petroleum Institute (API). The API gravity is based on the density of pure water which has an arbitrarily assigned API gravity value of 10^o (10 degrees). Oils with progressively lower specific gravities have higher API gravities. The following is the formula for calculating API gravity: API gravity = [141.5 ÷ (density at 15.5°C)] - 131.5. Oils with high densities have low API gravities and vice versa. In the United States, the price of a specific oil may be based on its API gravity as well as other properties of the oil.

Solubility in water is the measure of how much of a given oil will dissolve in the water column on a molecular basis. Solubility is important in that the soluble fractions of the oil are sometimes toxic to aquatic life, especially at higher concentrations. As the amount of oil lost to solubility is always small, this is not as great a loss mechanism as evaporation. In fact, the solubility of oil in water is so low (generally less than 100 parts per million) that it would be the equivalent of approximately one grain of sugar dissolving in a cup of water. Most bitumens have a very low solubility in water; however, Dilbits contain several soluble fractions. This is typically not sufficient, however, to cause fish toxicity except in confined waters.

The flash point of an oil is the temperature at which the liquid gives off sufficient vapours to ignite upon exposure to an open flame. A liquid is considered to be flammable if its flash point is less than 60°C. There is a broad range of flash points for oils and petroleum products, many of which are considered flammable, especially when fresh. Gasoline, which is flammable under all ambient conditions, poses a serious hazard when spilled. Many fresh crude oils have an abundance of volatile components and may be flammable for as long as one day until the more volatile components have evaporated. Dilbit can be flammable, whereas the bitumen is not at all.

The pour point of an oil is the temperature at which it takes longer than a specified time to pour from a standard measuring vessel. As oils are made up of hundreds of compounds, some of which may still be liquid at the pour point, the pour point is not the temperature at which the oil will no longer pour. The pour point represents a consistent temperature at which an oil will pour very slowly and therefore has limited use as an indicator of the state of the oil. In fact, pour point has been used too much in the past to predict how oils will behave in the environment. For example, waxy oils can have very low pour points, but may continue to spread slowly at that temperature and can evaporate to a significant degree. Because pour point is not the solidification point of oil, it is not the best predictor of how oil will behave or even more specifically, how it will move in the environment.

Distillation fractions represent the fraction of an oil (generally measured by volume) that is boiled off at a given temperature. This data is obtained on most crude oils so that oil companies can adjust parameters in their refineries to handle the oil. This data also provides environmentalists with useful insights into the chemical composition of oils. For example, while 70% of gasoline will boil off at 100ºC, only about 5% of a crude oil will boil off at that temperature and an even smaller amount of a typical bitumen. The distillation fractions correlate strongly to the composition of the oil and to other physical properties of the oil.

The oil/water interfacial tension, sometimes called surface tension, is the force of attraction or repulsion between the surface molecules of oil and water. Together with viscosity, surface tension is an indication of how rapidly and to what extent oil will spread on water. The lower the interfacial tension with water, the greater the extent of spreading. In actual practice, the interfacial tension must be considered along with the viscosity because it has been found that interfacial tension alone does not account for spreading behavior.

The vapour pressure is a measure of how the oil partitions between the liquid and gas phases, or how much vapour is in the space above a given amount of liquid oil at a fixed temperature. Because oils are a mixture of many compounds, the vapour pressure changes as the oil weathers. Vapour pressure is difficult to measure and is not frequently used to assess oil spills.

While there is a high correlation between the various oil properties, these correlations should be used cautiously as oils vary so much in composition (Jokuty et al., 1995). For example, the density of many oils can be predicted based on their viscosity. For other oils, however, this could result in errors. For example, waxy oils have much higher viscosities than would be implied from their densities. There are several mathematical equations for predicting one oil property from another property, but these must be used carefully as there are many exceptions.

The measurement of oil properties is an important consideration. While there are many standards for measuring fuel, e.g., ASTM, many of these standards are not applicable to crude oils and especially not to heavier bitumens and not to Dilbits. Similarly, many of the apparatuses for measurement are only appropriate for lighter fuels.

References:

Fingas, M.F., The Basics of Oil Spill Cleanup: Third Edition, CRC Press, Boca Raton, FL, 256 p, 2012.

Jokuty, P., M. Fingas, S. Whiticar, and B. Fieldhouse, "A Study of Viscosity and Interfacial Tension of Oils and Emulsions", Manuscript Report EE-153, Environmental Protection Service, Environment Canada, Ottawa, ON, 43 p, 1995.

1.3.5 Behavior of Diluted Bitumens

Oil spilled on water undergoes a series of changes in physical and chemical properties which in combination are termed 'weathering' (Fingas, 2012). Weathering processes occur at very different rates, but begin immediately after oil is spilled into the environment. Weathering rates are not consistent throughout the duration of an oil spill and are usually highest immediately after the spill.

Both weathering processes and the rates at which they occur often depend on the type of oil and then on environmental conditions. Most weathering processes are highly temperature-dependent, however, and will often slow to insignificant rates as temperatures approach freezing temperatures. The weathering processes include: evaporation, emulsification, natural dispersion, dissolution, photooxidation, sedimentation, adhesion to materials, interaction with mineral fines, biodegradation, and the formation of tar balls. These processes are listed in order of importance in terms of their effect on the percentage of total mass balance, i.e., the greatest loss from the slick in terms of percentage.

Evaporation is usually the most important weathering process. It has the greatest effect on the amount of oil remaining on water or land after a spill. Over a period of several days, a light fuel such as gasoline evaporates completely at temperatures above freezing, whereas only a small percentage of bitumen evaporates. The rate at which oil evaporates depends primarily on the oil's composition. The more volatile components an oil or fuel contains, the greater the extent and rate of its evaporation.

Oil and petroleum products evaporate in a slightly different manner than water and the process is much less dependent on wind speed and surface area. Oil evaporation can be considerably slowed down, however, by the formation of a 'crust' or 'skin' on top of the oil. This happens primarily on land where the oil layer is not agitated by water movement. The skin or crust is formed when the smaller compounds in the oil are removed, leaving the larger compounds, such as waxes and resins, at the surface. These components seal off the remainder of the oil and prevent evaporation. Stranded oil from old spills has been re-examined over many years and it has been found that there is no significant evaporation in the oil underneath the crust. When this crust has not formed, the same oil could be weathered to the hardness of wood.

Figure 3 This shows the high viscosity of Dilbit after about 9 days of weathering. The product has largely reverted to the original

bitumen by the evaporation of the diluent, condensate in this case.

The rate of evaporation is very rapid immediately after a spill and then slows considerably. About 80% of evaporation occurs in the first few days after a spill. The evaporation of most oils follows a logarithmic curve with time. Oil properties can change significantly with the extent of evaporation. If about 40% (by weight) of oil evaporates, its viscosity could increase by as much as a thousand-fold. Its density could rise by as much as 10% and its flash point by as much as 400%. In the case of Dilbits, the material will revert to largely the properties of the starting bitumen after weathering. The extent of evaporation can be the most important factor in determining properties of Dilbit at a given time after the spill, and in changing the behavior of the product.

Emulsification is the process by which one liquid is dispersed into another one in the form of small droplets. Water droplets can remain in an oil layer in a stable form and the resulting material is completely different. These water-in-oil emulsions are sometimes called 'mousse' or 'chocolate mousse' as they resemble this dessert. In fact, both the tastier version of chocolate mousse and butter are common examples of water-in-oil emulsions.

The mechanism of emulsion formation is not yet fully understood, but it probably starts with waves forcing the entry of small water droplets, about 10 to 25 µm (or 0.010 to 0.025 mm) in size, into the oil. If the oil is only slightly viscous, these small droplets will not leave the oil quickly. On the other hand, if the oil is too viscous, droplets will not enter the oil to any significant extent. Once in the oil, the droplets slowly gravitate to the bottom of the oil layer. Any asphaltenes and resins in the oil will interact with the water droplets to stabilize them. Depending on the quantity of asphaltenes and resins, as well as aromatic compounds that stabilize asphaltenes and resins in solution, an emulsion may be formed. The conditions required for emulsions of any stability to form may only be reached after a period of evaporation. Evaporation increased the amount of asphaltenes and resins in an oil compared to the other components, and increases the viscosity to the critical value.

Water can be present in oil in four ways. First, some oils contain about 1% water as soluble water. This water does not significantly change the physical or chemical properties of the oil. The second way is called 'entrainment', whereby water droplets are simply held in the oil by its viscosity to form an unstable emulsion. These are formed when water droplets are incorporated into oil by the sea's wave action and there are not enough asphaltenes and resins in the oil or if there is a high amount of aromatics in the oil which stabilizes the asphaltenes and resins, preventing them from acting on the water droplets. Unstable emulsions break down into water and oil within minutes or a few hours at most, once the sea energy diminishes. The properties and appearance of the unstable emulsion are almost the same as those of the starting oil, although the water droplets may be large enough to be seen with the naked eye. Dilbits can form entrained types if spilled onto turbulent water.

Meso-stable emulsions represent the third way water can be present in oil. These are formed when the small droplets of water are stabilized to a certain extent by a combination of the viscosity of the oil and the interfacial action of asphaltenes and resins. The viscosity of meso-stable emulsions is 20 to 80 times higher than that of the starting oil. These emulsions generally break down into oil and water or sometimes into water, oil, and residual emulsion within a few days. Semi- or meso-stable emulsions are viscous liquids that are reddish-brown or black in colour.

The fourth way that water exists in oil is in the form of stable emulsions. The viscosity of stable emulsions is 500 to 800 times higher than that of the starting oil and the emulsion will remain stable for weeks and even months after formation. Stable emulsions are reddish-brown in colour and appear to be nearly solid. Because of their high viscosity and near solidity, these emulsions do not spread and tend to remain in lumps or mats on the sea or shore.

The formation of emulsions is an important event in an oil spill. First, and most importantly, it substantially increases the actual volume of the spill. Emulsions of all types contain as much as 70% water and thus when emulsions are formed, the volume of the oil spill more than triples. Even more significantly, the viscosity of the oil increases by as much as 1000 times, depending on the type of emulsion formed.

These increases in volume and viscosity make cleanup operations more difficult. Emulsified oil is difficult or impossible to disperse, to recover with skimmers, or to burn. Emulsions can be broken down with special chemicals in order to recover the oil with skimmers or to burn it. It is thought that emulsions can break down into oil and water by further weathering, oxidation, and freeze-thaw action. Meso- or semi-stable emulsions are relatively easy to break down, whereas stable emulsions may take months or years to break down naturally.

Emulsion formation also changes the fate of the oil (Fingas and Fieldhouse, 2009). It has been noted that when oil forms stable or meso-stable emulsions, evaporation slows considerably. Biodegradation also appears to slow down. The dissolution of soluble components from oil may also cease once emulsification has occurred. The process of emulsion formation is discussed further in another issue.

Natural dispersion occurs when fine droplets of oil are transferred into the water column by wave action or turbulence. Small oil droplets (less than 20 µm or 0.020 mm) are relatively stable in water and will remain so for long periods of time. Large droplets tend to rise and larger droplets (more than 100 µm) will not stay in the water column for more than a few seconds. Depending on oil conditions and the amount of sea energy available, natural dispersion can be insignificant or it can remove some of the oil. It is felt that natural dispersion is not important to Dilbit fate.

Through the process of dissolution, some of the most soluble components of the oil are lost to the water under the slick. These include some of the lower molecular weight aromatics and some of the polar compounds, broadly categorized as resins. As only a small amount actually enters the water column, usually much less than a fraction of a percent of the oil, dissolution does not measurably change the mass balance of the oil. The significance of dissolution is that the soluble aromatic compounds are particularly toxic to fish and other aquatic life. If a spill of oil containing a large amount of soluble aromatic components occurs in shallow water and creates a high localized concentration of compounds, then significant numbers of aquatic organisms can be killed. Gasoline, diesel fuel, and light crude oils are the most likely to cause aquatic toxicity. A highly weathered oil is unlikely to dissolve into the water. Dissolution occurs immediately after the spill occurs and the rate of dissolution decreases rapidly after the spill as soluble substances are quickly depleted. Many of the soluble compounds also evaporate rapidly.

Photooxidation can change the oil composition. It occurs when the sun's action on an oil slick causes oxygen and carbons to combine and form new products that may be resins. The resins may be somewhat soluble and dissolve into the water or they may cause water-in-oil emulsions to form. It is not well understood how photooxidation specifically affects oils, although certain oils are susceptible to the process, while others are not. For most oils, photooxidation is not an important process in terms of changing their fate or mass balance after a spill.

Sedimentation is the process by which oil is deposited on the bottom of the water body. While the process itself is not well understood, certain facts about it are. Most sedimentation noted in the past has occurred when oil droplets reached a higher density than water after interacting with mineral matter in the water column. This interaction sometimes occurs on the shoreline or very close to the shore. Once oil is on the bottom, it is usually covered by other sediment and degrades very slowly. In a few well-studied spills, a significant amount (about 10%) of the oil was sedimented on the sea floor. Such amounts can be harmful to biota that inevitably come in contact with the oil on the sea bottom.

Oil is very adhesive, especially when it is moderately weathered, and binds to shoreline materials or other mineral material with which it comes in contact. A significant amount of oil can be left in the environment after a spill in the form of residual amounts adhering to shorelines and man-made structures such as piers and artificial shorelines. As this oil usually contains a high percentage of aromatics and asphaltenes with high molecular weight, it does not degrade significantly and can remain in the environment for decades.

Oil slicks and oil on shorelines sometimes interact with mineral fines suspended in the water column and the oil is thereby transferred to the water column. Particles of mineral with oil attached may be heavier than water and sink to the bottom as sediment or the oil may detach and refloat.

A large number of microorganisms are capable of degrading petroleum hydrocarbons. Many species of bacteria, fungi, and yeasts metabolize petroleum hydrocarbons as a food energy source. Bacteria and other degrading organisms are most abundant on land in areas where there have been petroleum seeps, although these microorganisms are found everywhere in the environment. As each species can utilize only a few related compounds at most, however, broad-spectrum degradation does not occur. Hydrocarbons metabolized by microorganisms are generally converted to an oxidized compound, which may be further degraded, may be soluble, or may accumulate in the remaining oil. The aquatic toxicity of the biodegradation products is sometimes greater than that of the parent compounds.

The rate of biodegradation is greatest on saturates, particularly those containing approximately 12 to 20 carbons (Haus et al., 2004). Aromatics and asphaltenes that have a high molecular weight, biodegrade very slowly, if at all. This explains the durability of roof shingles containing tar and roads made of asphalt, as both tar and asphalt consist primarily of aromatics and asphaltenes. Bitumen contain little material that is readily biodegradable.

Tar balls are agglomerations of thick oil less than about 10 cm in diameter. Larger accumulations of the same material ranging from about 10 cm to 1 m in diameter are called tar mats. Tar mats are pancake-shaped, rather than round. Their formation is still not completely understood, but it is known that they are formed from the residuals of heavy crudes. After these oils weather and slicks are broken up, the residuals remain in tar balls or tar mats. The reformation of droplets into tar balls and tar mats has also been observed, with the binding force being simply adhesion. The formation of tar balls is the ultimate fate of many oils. These tar balls are then deposited on shorelines.

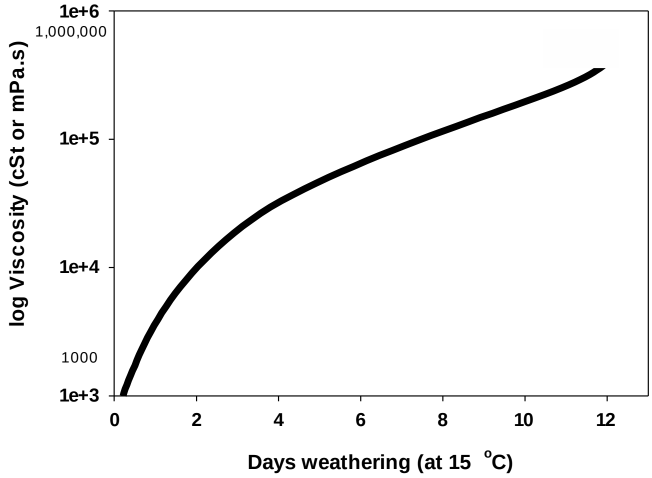
References:

Fingas, M.F., The Basics of Oil Spill Cleanup: Third Edition, CRC Press, Boca Raton, FL, 256 p, 2012.

Haus, F., O. Boissel, and G.-A. Junter, "Primary and Ultimate Biodegradabilities of Mineral- based Oils and their Relationships with Oil Viscosity", International Biodeterioration and Biodegradation, Vol. 54, pp 189-192, 2004.

2. Evaporation of Dilbits

Evaporation is particularly important for Dilbits. The light ends of Dilbit evaporate leaving the denser and more viscous bitumen behind. There exists laboratory data and small test tank data on the weathering of Dilbits (ESTC, 2014; Fed Gov, 2013; Witt O'Briens, 2013). This data was compared and the equivalent viscosity and density were compared for % weathered and time and the scale then approximated over days rather than % weathered. This was done to provide a practical base for spill countermeasures. It must be noted that the data are for temperatures at 15ºC. It would take approximately twice as long to weather at about 0 to 5ºC and half as long at temperatures of about 30ºC. The estimated viscosity and density changes with weathering are shown in Figures 4 to 9.



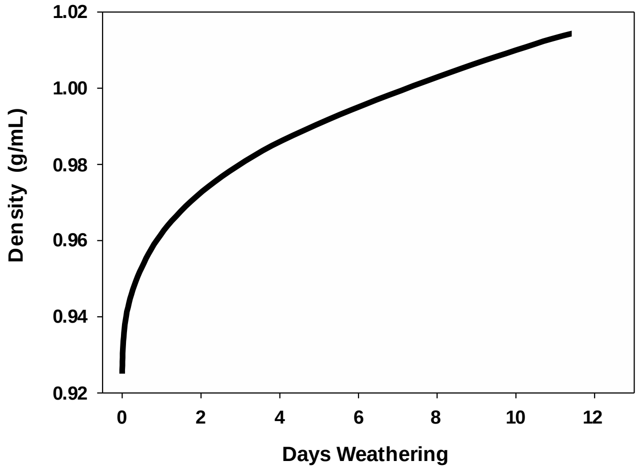
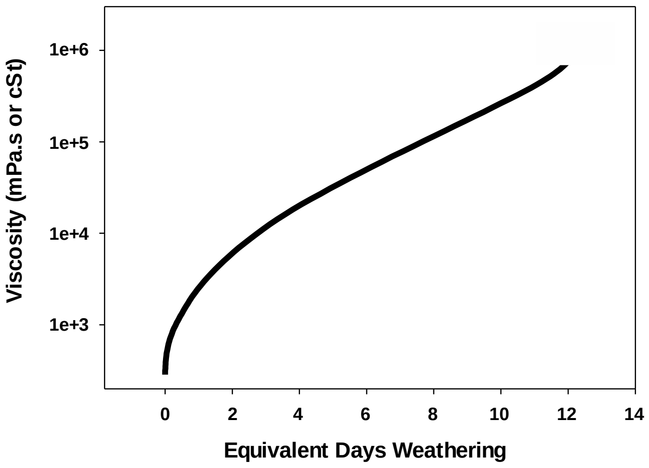


Figure 4 Viscosity of Access Western Blend with weathering time of the corresponding Dilbit

Figure 5 Density of Access Western Blend with weathering time of the corresponding Dilbit



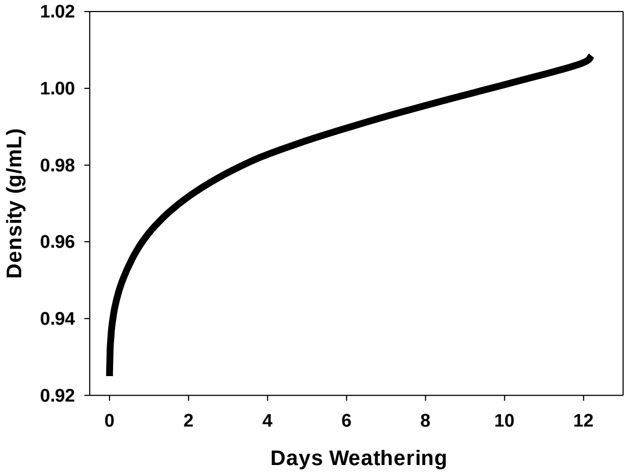
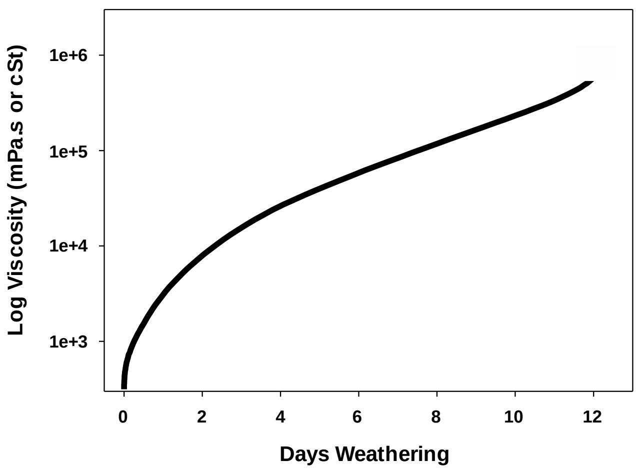


Figure 6 Viscosity of Cold Lake Dilbit with weathering time of the corresponding Dilbit

Figure 7 Density of Cold Lake Dilbit with weathering time of the corresponding Dilbit



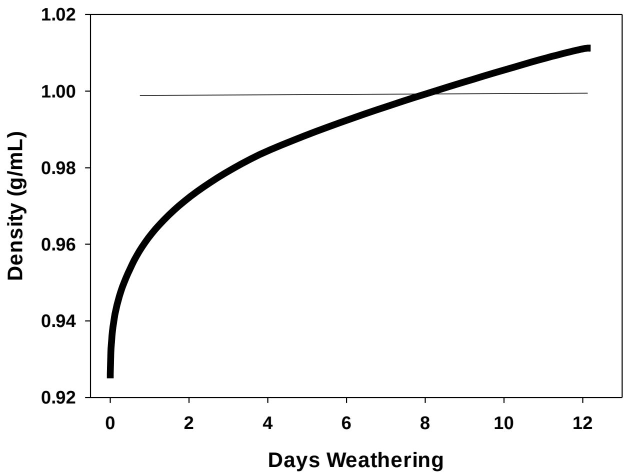


Figure 8 Viscosity of a typical Dilbit with weathering time *Figure 9 Density of a typical Dilbit with weathering time*

Figures 4 to 9 were based on direct weathering in laboratories and in small tanks. For C4/C6 enhanced Dilbit and Synbit, data are more difficult to find and must be estimated from small experiments. Figures 4 to 9 are calculated using data obtained at 15ºC. At double the temperature the changes would occur in about half of the time and at lower temperatures (0 to 5ºC), these changes could take up to twice the time.

References:

ESTC (Environmental Technology Centre), World Catalogue of Oil Properties, WWW.ETC-CTE.ec.gc.ca, 2014.
Fed Gov, Properties, Composition and Marine Spill Behavior, Fate and Transport of Two Diluted Bitumen Products from the Canadian Oil Sands, Government of Canada, 2013
Witt O'Briens, Dilbit Fate and Behavior, Report of the Gainford Trials, 2013

Evaporation is particularly important for Dilbits and Synbits. The diluent or lighter ends from these products evaporate leaving the denser and more viscous bitumen behind. There are some data on the Synbits enabling one to predict their behavior once released into the environment. The graphs that follow show the behavior of weathering Synbits. One will note that this is quite different from the resulting behaviour of Dilbits, as the weathered products of Synbits are less viscous and less dense with the same amount of weathering.

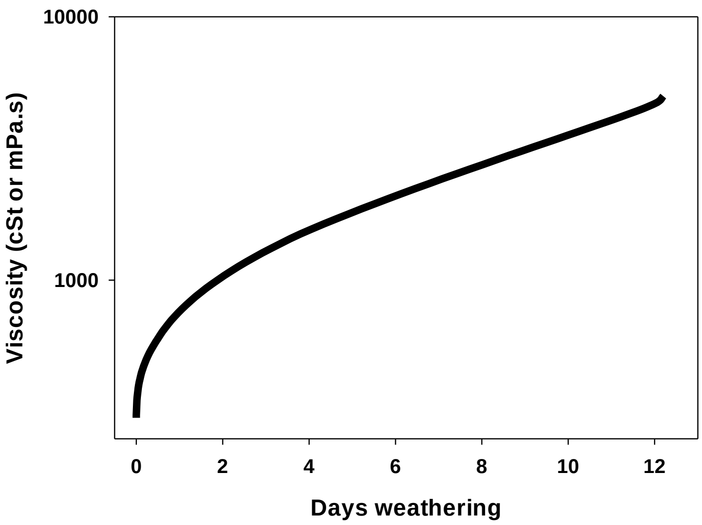


Figure 10 Viscosity of a Synbit as it weathers

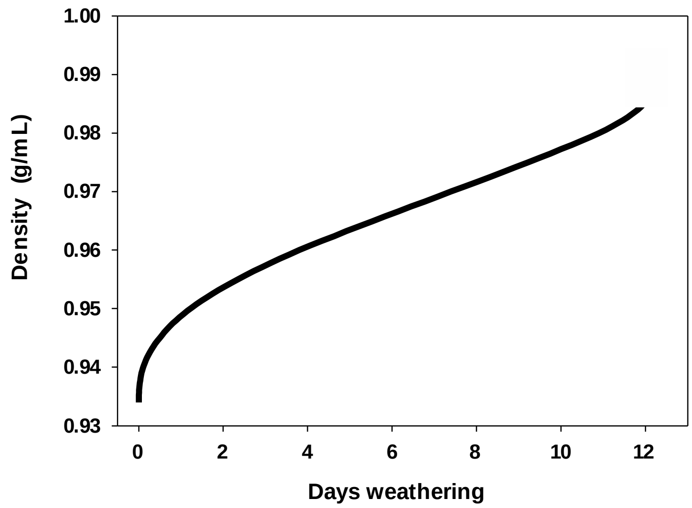


Figure 11 Predicted Density of a Synbit as it weathers

Figures 10 and 11 are calculated using data obtained at 15ºC. At double the temperature the changes would occur in about half of the time and at lower temperatures (0 to 5ºC), these changes could take up to twice the time.

3 Flammability of Dilbits

An issue that is important to health and safety is that of flammability. The Dilbits when released, can be flammable, especially those enhanced with C4 or C5. This is shown in Figures 12 to 14.

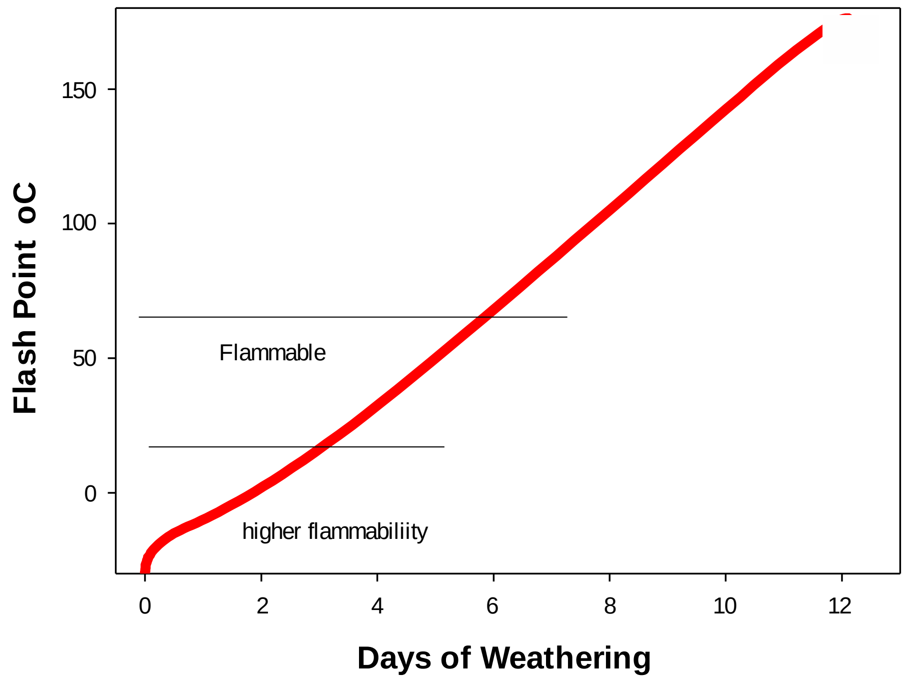


Figure 12 The flammability of a Dilbit from laboratory data over a period of days.

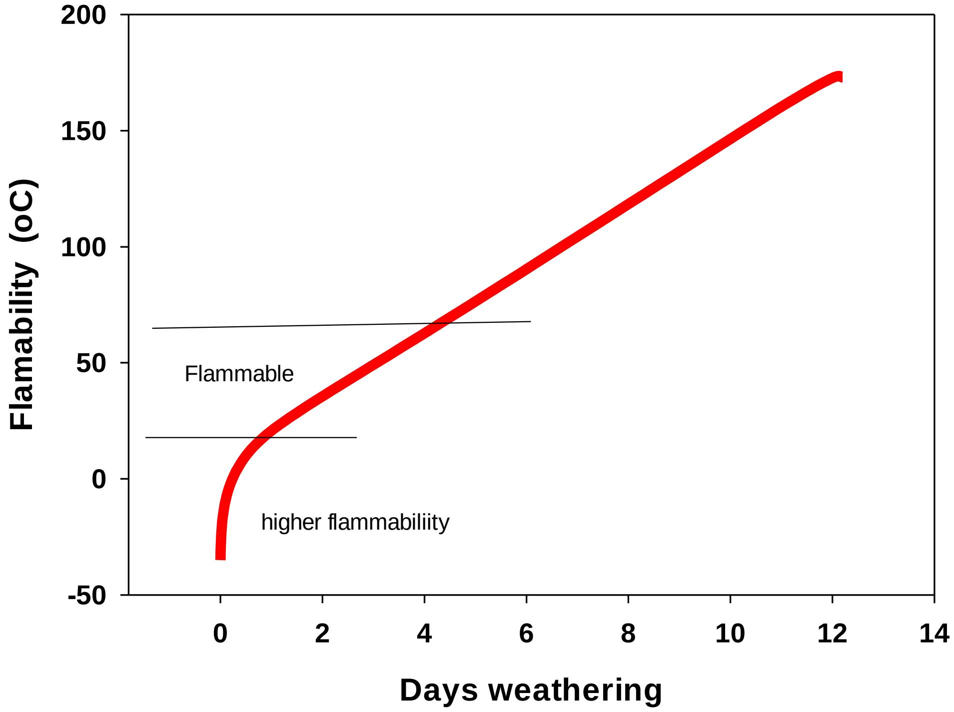


Figure 13 Predicted flammability of a C4/C5 enhanced Dilbit

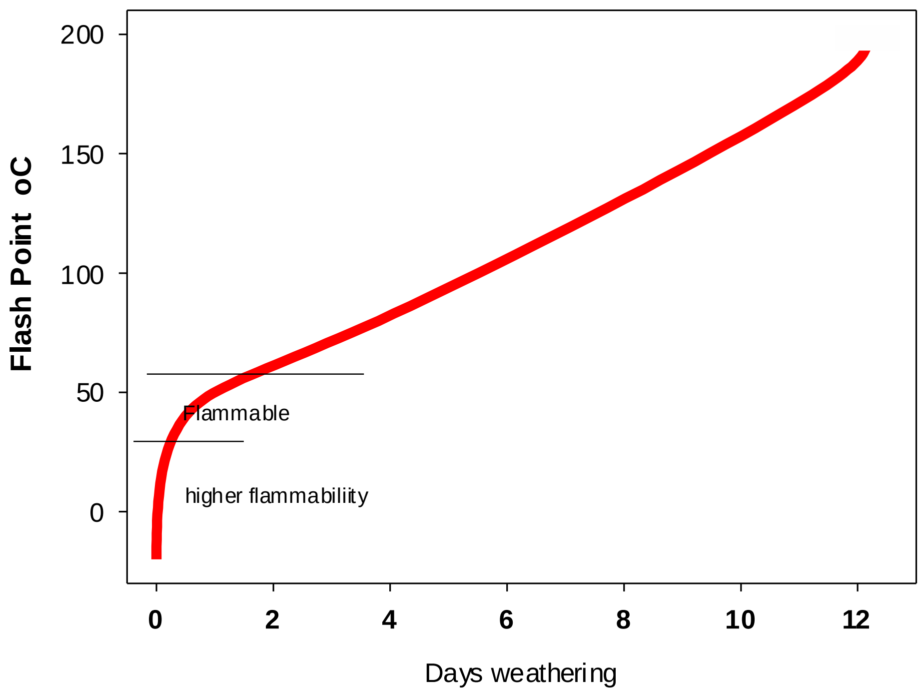


Figure 14 The predicted flammability of a Synbit

This indicates that standard Dilbits can pose a flammability hazard up to a few days after the spill. Enhanced C4 Dilbits will pose a greater hazard, but for a shorter time. Cleanup crews are advised to use explosimeters in dealing with Dilbit spills.

4. Emulsion Formation

Water-in-oil emulsions sometimes form after oil products are spilled. These emulsions, often called “chocolate mousse” or “mousse” by oil spill workers, can make the cleanup of oil spills very difficult. When water-in-oil emulsions form, the physical properties of oil changes dramatically. As an example, stable emulsions contain 60 to 80% water, thus expanding the spilled material from 2 to 5 times the original volume. Most importantly, the viscosity of the oil typically changes from a few hundred mPa.s to about 100,000 mPa.s, an increase by a factor of 500 to 1000. A liquid product is changed into a heavy, semi-solid material. These emulsions are difficult to recover with ordinary spill recovery equipment.

Many researchers feel that emulsification is the second most important behavioral characteristic of oil after evaporation. Emulsification has a significant effect on the behavior of oil spills at sea. As a result of emulsification, evaporation of oil spills slows by orders-of-magnitude, spreading slows by similar rates, and the oil rides lower in the water column, showing different drag with respect to the wind. Emulsification also significantly affects other aspects of a spill, such as cleanup response. Spill countermeasures are quite different for emulsions as they are hard to recover mechanically, to treat, or to burn.

There are four clearly-defined water-in-oil types are formed by crude oil when mixed with water (Fingas and Fieldhouse, 2009). This was shown by water resolution over time, by a number of rheological measurements, and by the water-in-oil product’s visual appearance, both on the day of formation and one week later. Some emulsions were observed for over a year, with the same results. The types are named stable water-in-oil emulsions, meso-stable water-in-oil emulsions, entrained water, and unstable water-in-oil types. The differences among the four types are quite large and are based on at least two water content measurements and five rheological measurements. More than 400 oils or petroleum products were studied.

Bitumen and weathered Dilbits do not form emulsions. Lightly-weathered Dilbits can entrain water droplets in turbulent water conditions.

Stable emulsions are reddish-brown semi-solid substances with an average water content of about 70-80% on the day of formation and about the same one week later. Stable emulsions remain stable for at least 4 weeks under laboratory conditions. All of the stable emulsions studied remained so for at least one year. The viscosity increase following formation averages 400 times the original viscosity and one week later averages 850 times the original viscosity.

Meso-stable water-in-oil emulsions are reddish-brown viscous liquids with an average water content of 60-65% on the first day of formation and less than 30% one week later. Meso-stable emulsions generally break down to about 20% water content within one week. The viscosity increases over the initial viscosity on the day of formation averages a factor of 7 and one week later averages 5.

Entrained water-in-oil types are black viscous liquids with an average water content of 40-50% on the first day of formation and less than 28% one week later. The viscosity increase over the day of formation averages a multiple of two and one week later still averages two. Entrained water-in-oil types appear to be applicable to viscous oils and petroleum products, but not extremely viscous products. Dilbits will form entrained water-in-oil types given high levels of water mixing.

Unstable water-in-oil emulsion types or those oils that do not form any of the other three types are characterized by the fact that the oil does not hold significant amounts of water following mixing with water. There is a much broader range of properties in the starting oil than for the other three water-in-oil states.

Stable emulsions, on average, begin at a high level of water content (about 75%) and lose little water over one year. Meso-stable emulsions, on the other hand, begin at about 65% and lose most of this water within a few days. Entrained water-in-oil types pick up only about 40% water and only slowly lose this over one year. Unstable water-in-oil types pick up only a few percent of water and this does not change much over one year. The apparent viscosity of stable emulsion increases over the period of one year and the others generally decline or only increase a small amount. Thus, after a few months, the stable emulsion will have the greatest viscosity. The stable emulsion has about the same viscous and elastic components over the year. All other water-in-oil types show a much greater viscous component than the elastic component.

If the viscosity of the oil is too high, water droplets cannot penetrate the oil mass to a great extent and thus emulsions are not formed. At moderate oil viscosities, about 1000 to 10,000 mPa.s, the water droplets may be retained by viscosity alone. This is felt to be the origin of the entrained water-in-oil type. Bitumen and weathered Dilbits do not form emulsions. Lightly-weathered Dilbits can entrain water droplets in turbulent water conditions.

5 Dispersant Effectiveness and Shoreline Cleaning Agents

Tests have shown that Dilbits show little chemical dispersibility, especially once weathered more than a few hours (Witt O’Briens, 2013).

Tests on oiled tiles shows that Corexit EC9580 is effective for cleaning Dilbit up to about 5 days in the sun and 7 days after oiling. After this time, the bitumen is hard to remove. These and other tests are shown in Figures 15 to 17.

Figure 15 Test of weathered Dilbit gravel penetration – Gainford Tests – May 2013

Figure 16 Removal tests of weathered Dilbit from ceramic tokens – Gainford tests, May 2013

Figure 17 Successful removal of Dilbit weathered for 4 days

Reference:
Witt O'Briens, *Dilbit Fate and Behavior, Report of the Gainford Trials*, 2013

6. Skimming

Tests on skimming spilled Dilbit shows the following:

- Initially the product behaves like a medium crude
- Skimmers that have interchangeable disks and brushes are best run initially with disks and then after about a few days with brushes
- The recovery rates and water/oil ratios are about the same as medium crude in the first few days and like that of heavy oil thereafter (Witt O'Briens, 2013). Figures 18 to 20 illustrate some of this testing.

Figure 18 A Lamor skimmer operating during a weathered Dilbit recover test

Figure 19   Skimmer test carried out at Gainford, Alberta, 2013

Figure 20 Aqua-Guard Skimmer working at Gainford Trials, May 2013

7. Burning

Burning is a countermeasure that can be applied to Dilbit spills. Freshly-spilled Dilbit burns similar to a light or medium crude oil, while more weathered Dilbit burns similar to a heavy oil. Tests show that the ease of ignition is also similar to these comparison oils. Figure 21 shows a burn of weathered Dilbit.

Figure 21 A test burn of weathered Dilbit

Reference:
Witt O'Briens, *Dilbit Fate and Behavior, Report of the Gainford Trials*, 2013

8 Summary

Diluted bitumens are Alberta oil sands bitumen diluted either by condensate, C4/C5 enhanced condensate, naphtha (Dilbit) or synthetic crude oil (Synbit). Once spilled the Dilbits return to the properties of the starting bitumen as the volatile components evaporate. A spilled Synbit does not return to the properties of the starting bitumen, but rather weathers to a heavier oil, moderating properties between a weathered synthetic crude and a bitumen. Figure 22 shows the typical viscosity change for each type and Figure 23 shows the density change for the three products.

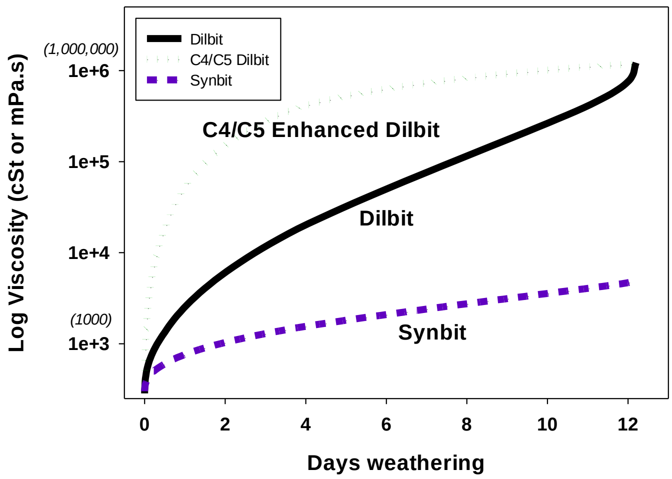


Figure 22   The typical viscosity changes for the three types of diluted bitumens. These are calculated at 15ºC. The changes would be about twice as rapid at about twice the temperature and about half as large at half the temperature or lower. Figure 22 shows that Dilbits revert to close to the viscosity of the starting bitumen after about one and a half weeks at 15ºC. Synbit, on the other hand just changes to viscous heavy oil.

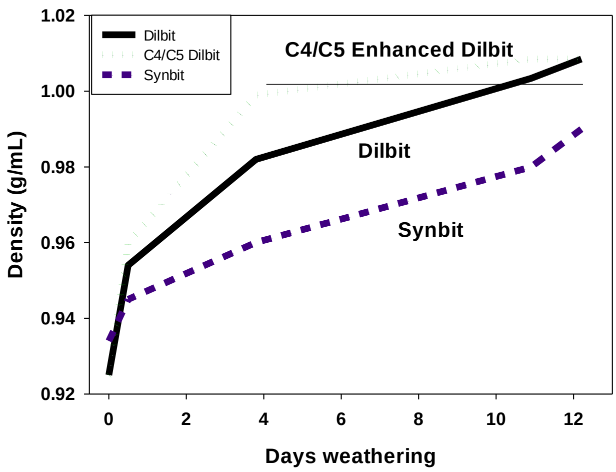


Figure 23 The density changes for the three types of diluted bitumens. These are calculated at 15ºC. The changes would be about twice as rapid at about twice the temperature and about half as large at half the temperature or lower. Figure 23 shows that Dilbits revert to close to the density of the starting bitumen after about one and a half weeks at 15ºC. Synbit, on the other hand changes to a viscous heavy oil.

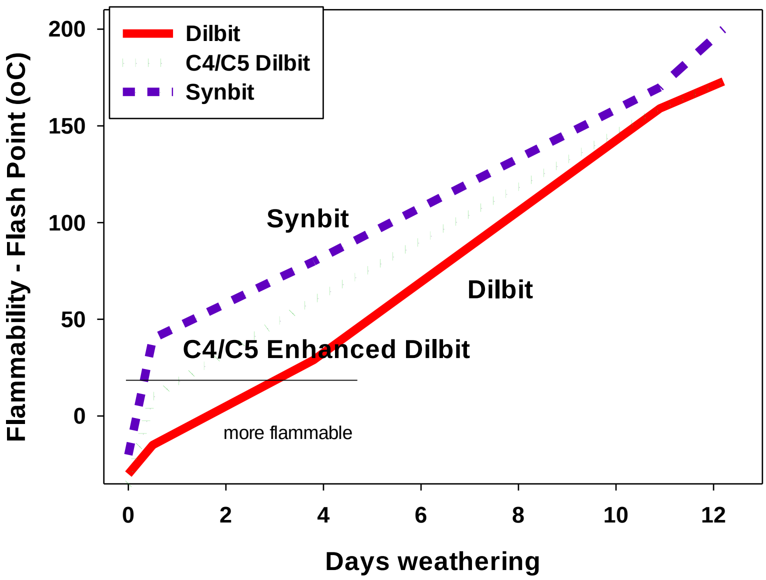


Figure 24 The flammability (flash point) changes for the three types of diluted bitumens as these weather. This shows that C4/C5 enhanced Dilbit is the most flammable product but for only about one day of exposure. Regular Dilbit is flammable for about 2 days and Synbit for about half a day after the spill.

It was found that when initially spilled all three products can form entrained water mixtures in turbulent waters. After weathering, Dilbits are too viscous to form such products. Entrained water types would break down naturally after a time once the turbulence is removed. In inland waters emulsification is rare.

Spill countermeasures for spilled Dilbits and Synbits can proceed with either skimming and/or in-situ burning.

Initially when spilled, Dilbits require a regular skimmer and later a heavy oil skimmer. Synbits are similar, however the regular skimmers might be used throughout the cleanup cycle. Only after extensive weathering are heavy oil skimmers required for Synbit spills.

On shorelines or solid surfaces, EC 9580 works until the product is weathered more than 5 days. High pressure washing is effective until the products weather longer than about a week. Oiled surfaces may be a challenge to clean up.

Table 6 Summary Properties of Diluted Bitumens

Diluted Product	Diluent	Starting Viscosity	Ending Viscosity*	Starting Density	Ending Density*	Days product is flammable**
Dilbit	gas condensate	~ 300 cSt	~1,000,000	0.93 g/mL	1 or >1	2 days
Dilbit	synthetic naphtha	~ 300 cSt	~1,000,000	0.93 g/mL	1 or >1	2 - 3 days
C4/C5 enhanced Dilbit	butane/pentane enhanced condensate	~ 300 cSt	~1,000,000	0.93 g/mL	1 or >1	1 day
Synbit	synthetic crude	~ 300 cSt	~5,000	0.93 g/mL	~0.98	1/2 day
Dilsynbit	synthetic crude & gas condensate	~ 300 cSt	~8,000	0.93 g/mL	~0.98	1/2 day

** Ending properties are estimated after about 2 weeks of weathering*

*** Estimated using typical weathering characteristics after a spill*

Definitions

Bitumen – heavy oil from oil sands
Condensate – a light oil product typically produced from gas wells and used as a diluent for transporting bitumen products
Dilbit – diluted bitumen with about 30% diluent, typically transported by pipeline
Dilsynbit – diluted bitumen with synthetic crude and another diluent – usually condensate
Diluent – traditionally condensate but could be a variety of materials
Neatbit – undiluted bitumen, if shipped would be shipped by heated rail tank cars
Railbit – diluted bitumen with about 15% diluent, typically shipped by rail tank car
Synbit – bitumen diluted with synthetic crude
Synthetic crude – refined oil from bitumen, refined to the extent it resembles crude oil
Dilsynbit – diluted bitumen with synthetic crude and another diluent – usually condensate