Skye Petroleum, Inc

Deposit Removal

Uses of Skye Petroleum Skye Chem Products for the Removal of Petroleum Deposits in Production and Storage.

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Problems of Organic Deposits

Introduction

Organic deposits are formed during production and storage of crude oil. The presence of these deposits in a storage tank or oil well is both an economic liability and an engineering challenge.

Organic deposits or sludge that occur in storage occupy usable tank storage space, reducing the available capacity and decreasing system throughputs. The amount of capacity reduction can be surprising. Table 1 shows the volume occupied by various sludge depths.

Table 1 Sludge Volume based on Tank Diameter

Tank Diameter		Sludge Depth		Volume of Sludge	
ft.	m	ft.	m	bbl.	m^3
100	30.5	1	0.3048	1399	223
		2	0.6096	2798	446
		3	0.9144	4197	669
150	45.7	1	0.3048	3147	501
		2	0.6096	6294	1002
		3	0.9144	9441	1503
300	91.4	1	0.3048	12589	2005
		2	0.6096	25178	4010
		3	0.9144	37767	6015

This volume of sludge represents an economic liability in two ways. First, the sludge occupies space in the tank that could otherwise be used for more valuable product. Second, the sludge is a bi-product of the oil placed in the tank. That is, if one percent of each barrel of oil becomes sludge, then the sludge represents a loss of 1% of the value of the oil originally placed in the tank.

Finally, sludge also poses a problem for inspection and maintenance. Sludge is a layer of un-pumpable materials, which must be removed before preventive maintenance, or inspection can be performed.

Deposits in oil production can act in several ways to reduce flows. The presence of the deposit will cause blockage of pore throats in oil and gas production. Flow restrictions on fracture faces and sand packs, reduction of pipe volume, hindrance of pump rods and blocking of pumps, and a decrease in pipeline volume similar to the problems encountered in storage tanks. The removal of the deposit or its prevention can greatly improve the volume of production and reduce the energy required in pumping and lift.

What is Nature of Organic Fouling Found in Crude production

Deposits generated in oil production can contain as many as five distinct phases.

1. **Crude Oil**
2. **Water in Oil emulsion**
3. **Free Water**
4. **Wax or Sludge**
5. **Inorganic solids**

Sludge is a general term used to describe the residual deposits found at the bottom of tanks and other storage vessels. Wax is a term used on the downhole and produced fluids including oil production pipelines. Wax is often incorrectly used to describe any organic deposit found in a production system. In oil production wax can be anything from a soft deposit to a hard residue. Sludges form from both raw crude and processed oil. The physical nature of each deposit varies, but in general, they usually occur as viscous semi-solids composed of a mixture of water, light hydrocarbons, waxes, asphaltenes, and sometimes-inorganic solids such as sand, iron sulphides and iron oxides.

In the course of evaluating various sludges from around the world, we have determined a typical compositional profile for sludge coming from crude oil. The physical properties for these sludges are given in the table below:

Table 2 Typical Sludge properties

Wax	10 – 40%
Asphaltenes	1 - 10%
Water	0 – 10%
Inorganic solids	0 - 5%
Light Hydrocarbons	40 – 80%
Viscosity	60 – 50000 cP
Cloud Point	35 – 45°C
Pour Point	30 – 80°C

For the most part, the four critical properties of sludge are the wax content, asphaltene content, pour point and cloud points.

Deposits form when a crude oil's properties are changed due to changes in external conditions. Cooling below the cloud point, mixing with incompatible materials, and the introduction of water to form emulsions make up the most common causes for sludge formation. The precipitate that forms is often enriched in the second phase materials - waxes, water, solids, and asphaltenes.

Characterization of a Deposit

An analysis to determine the composition of sludge is an important first step in determining the most efficient means to removing it. The analysis may consist of the following steps:

- **Wax, asphaltene and residue determination**
- **Water content**
- **Viscosity profile (including cloud point and pour point)**

Wax, Asphaltene and Residue Determination

This method of determining the composition of a deposit depends on the relative solubility differences of the components to be determined. The method uses boiling isopropanol to separate light hydrocarbons such as short chain hydrocarbons, cyclic hydrocarbons and aromatic hydrocarbons as well as the waxes from the high molecular weight asphaltenes and the other residues. Waxes are hydrocarbons with a chain length longer than C_{12}-C_{14} and potentially as long as C_{60}. Waxes are typically soluble in low surface tension solvents such as pentane or hexane but not in high surface tension solvents such as water or methanol. However, at higher temperatures waxes can be induced to form a solution with isopropanol, separating them from the asphaltenes and residues. Waxes are not soluble in isopropanol at lower temperatures and thus can be separated from the lighter materials by precipitation.

Asphaltenes are large complex aromatic molecules[i]. Residues are those materials that are not soluble in most organic solvents and typically include inorganic solids (such as iron oxide, iron sulphides and sand), sulphur, coal and coke. The asphaltenes can be extracted from the residues using a solvent such as chloroform or toluene.

Water Content

The amount of water tied up in a deposit is often not easy to determine by conventional means. The typical method – using a centrifuge to separate the water will often give inaccurate values due to hang up of the water in the extremely high viscosity of the sludge. Several methods can be used to overcome this problem. The first is analysis of the sludge using a Dean Stark extraction. The second uses a Karl Fischer titration, and finally, water can be determined by centrifuging a sample that has been diluted as much as ten to one with a suitable solvent such as xylene or toluene.

Viscosity Profile

The viscosity profile of a sludge is a way of describing how the viscosity of the sludge varies with temperature. The viscosity of most liquids will increase with decreasing temperature. In the case of a pure substance the change of viscosity with temperature can be described by the empirical formula:

$$\mu = Ae^{B/T}$$

Where A and B can be determined by plotting the log of the viscosity (log μ) versus 1/T.

Unfortunately, hydrocarbon sludges are not pure substances. As the solution cools, a second solid phase will precipitate from the liquid. At this point, the rate of change of the viscosity with temperature ($\delta\mu/\delta T$) will change to reflect the presence of the solid phase.

When a second phase is present the viscosity of the solution is proportional to the volume fraction of the second phase. This reflects the growth of the wax crystals or the agglomeration of asphaltenes as the sample cools. Growing crystals will give an increasing viscosity as the volume occupied by the crystals increases.

The final component to sludge viscosity is the interaction of the particles in the sludge with each other. Waxes present in crude oil come in two varieties. The first, called macrocrystalline wax is composed of paraffinic hydrocarbons (C16-C36), and the second, called microcrystalline wax, is composed of naphthenic hydrocarbons (C30 – C60). Either type of wax molecule will form crystals upon cooling, which will interact with each other. This interaction leads to thixotropy. That is, the solution's response to shear rate is non-Newtonian. A Newtonian fluid has a linear response to shear rate; the viscosity remains the same at all shear rates. A thixotropic fluid has a lower viscosity at higher shear rates, and a high viscosity at low shear rates. Thus, the fluid could be said to be shear thinning.

Measurements using a variable shear rate viscometer are necessary to determine if a sludge is shear sensitive.

Wax Dispersants – Mechanisms of Action for Skye Chem WD

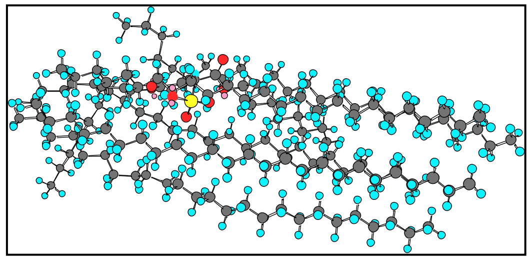


Figure 1 Wax Crystal with Dispersant molecule

The viscosity of a mixture is often due to the presence of an internal phase. The interaction particles such as wax crystals or water droplets (in the case of an emulsion) are generally accepted to be the source of the viscosity of such systems. In the case where waxes form the internal phase, smaller particles will interact to form an interconnecting matrix, entrapping other materials such as water and inorganic solids. The combination of the matrix effect and the interaction of the smaller particles lead this form of deposit to have a higher viscosity than could be explained by the presence of the second phase by itself.

The presence of the wax crystal matrix also makes the deposits and sludges thixotropic. That is, the deposit or sludge has a high viscosity when measured at a low shear rate and a much lower viscosity, when measured at a high shear rate. This type of sludge also exhibits a hysteresis; the properties of the material will change with its shear history.

This type of behavior results when the weaker electrostatic bonds that make up the matrix of crystals are broken by mixing the sludge at a high shear rate. The bulk viscosity of the fluid will be reduced and after the bonds have been broken the sludge may remain fluid (or having a lower measurable viscosity) at low shear rates. Given time, however, the network will reform and the low shear rate viscosity will reappear.

The fact that sludge with this kind of structure can be made pumpable at some arbitrarily high shear rate has been exploited by some to help remove sludges. The sludge is mixed at high shear with a sufficient volume of solvent. Two problems occur with this approach. First, the volume and composition of the solvent must be adequate to prevent reforming of the sludge. Second, the entire sludge volume must be sheared at a high rate in order for mixing to occur. Dead spots or unprocessed sludge will still possess the original high viscosity properties.

Dispersants have a different effect on sludge. First, the dispersant acts to change the electrostatic charge on the wax crystal particles. This charge is technically described as the zeta potential. By making the wax particles take on a new charge, the particles will repel each other, making the formation and maintenance of the crystal matrix difficult (and hopefully, impossible). The dispersant in effect acts as an electrostatic wedge prying the agglomerated crystals apart.

Energy in the form of sheer is needed to disperse a sludge or deposit. The amount of energy required is proportional to the Van der Waal forces that must be overcome when the wax crystals in a sludge or deposit are torn apart. This energy is required in addition to the amount of energy required to move a static liquid. Skye Chem WD acts in two ways. One of the surfactants in Skye Chem WD acts as a wedge to initiate the opening of a "crack" or fracture between the wax crystal surfaces. The presence of this crack lowers the amount of energy required to create the new free wax crystal surface. By lowering the amount of energy required it becomes possible to easily disperse the waxes using lower pressures and flow velocities.

A second set of surfactants in Skye Chem WD then acts on the wax surfaces, modifying them to have a net negative charge. The wax crystals now repel each other. The repulsion between the crystals prevents their precipitation, keeping them suspended. This action can also significantly lower the pour point and viscosity of a mixture making it easier to pump and handle.

The net physical effect of the dispersant is to make the viscosity of the fluid at low shear rates resemble the viscosity of the fluid at high shear rates, eliminating the thixotropic properties of the fluid. In addition, once sheared the fluid does not return to its old viscosity.

The second effect of the dispersants is to make the particles more soluble in the bulk fluid. This is accomplished by using dispersant surfactants that, when associated with the solids, will make the surfaces of the solids more amenable to wetting by the solvent. This effect applies to all types of internal phases including asphaltenes, waxes, inorganic solids and water. By wetting the solids with the solvents, the solids disperse better, and their interaction is inhibited because they are farther apart.

Finally the addition of crystal modifiers to the WD product prevents secondary reprecipitation of organic deposits after the conditions have changed sufficiently that the wax in the deposit would ordinarily crystalize back out. This allows effective transport of the dissolved deposit out of the reservoir or flow system.

Asphaltenes and Resins

Asphaltenes are the component of heavy oil responsible for much of the viscosity. By the classical definition, asphaltenes are the fraction of crude oil that is precipitated by low surface tension solvents such as pentane or hexane. The actual chemical makeup of asphaltenes is complex. Asphaltenes do not crystallize and cannot be separated into narrow fractions by composition. Thus, any evaluation of asphaltenes is a description of a range of structures and isomers. Postulated structures of asphaltenes generally illustrate asphaltene as a series of condensed aromatic

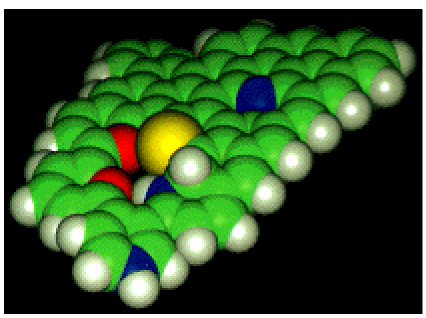
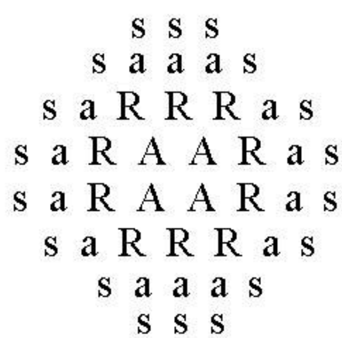


Figure 2 Asphaltene Molecule

rings incorporating sulphur, nitrogen and oxygen atoms. The actual structure of asphaltenes in a particular crude oil is undoubtedly a mixture of many molecules ranging in molecular weight from a few hundred grams per mole to Nano aggregates of several thousand[ii].

Resins are the other group of compounds that are precipitated when low surface tension solvents are added to crude oil. Resins are thought to have structures much like asphaltenes, but have a lower molecular weight.

The actual physical chemistry of asphaltenes in solution is a matter of debate. Asphaltenes are thought to exist as colloidal Nano aggregates of smaller particles surrounded by resins, which act to provide a transition between the non-polar oil and the polar asphaltenes. One suggestion is asphaltenes are associated in small clusters bound together by pi-cloud interactions occurring between the aromatic rings that make up the asphaltene molecules[iii].



A = Asphaltenes (solute)
R = Resins (dispersant)
a = Small Ring Aromatics (solvent)
s = Saturates (nonsolvent)

A second hypothesis is that asphaltenes associate with each other due to the strength of their Van der Waals forces, which is aided by their relative insolubility within the bulk solution.

Effect of Asphaltenes on the Viscosity of Heavy Oil or Sludge

In either model the presence of resins in the asphaltene/oil system is critical to the maintenance of asphaltenes as independent small particles. Asphaltenes contribute to the viscosity of heavy oil in two ways.

First, asphaltene molecules form small aggregates which can be built into larger and larger fractal structures based on the smaller aggregates, these act as a second internal phase dispersed in the oil. This second phase increases the viscosity of the system proportionally to the volume occupied by the phase. Shear (that is flow), changes in temperature and pressure, as well as changes to the chemistry of the oil due to release of light ends, can act to further increase the size of asphaltene micelles – increasing the viscosity of the oil as it is produced.

Second, asphaltenes and resins are highly polar molecules having a higher affinity for the water phase of oil field emulsions than the oil itself. This tends to cause the accumulation of asphaltenes at the oil water interface of the emulsion droplets – stabilising the emulsions, and making them difficult to break. The emulsified oil is even more viscous than the heavy oil itself.

Asphaltene Dispersants - Mechanism of Action for Skye Chem AD

Skye Chem AD is a large organic molecule, with a charged hydrophilic aromatic end, balanced by a long chained aliphatic hydrophobic end. The molecule is designed to resemble the resin portion of heavy oil.

Skye Chem AD acts to improve the stabilization of asphaltenes and maintain their dispersion in solution. It does this by providing increased stability to small asphaltene aggregates, inhibiting their condensation into large structures. The Skye Chem AD molecule is incorporated into the asphaltenes and improves the asphaltene aggregates dispensability in the oil.

Two effects of Skye Chem AD have been observed. The first is a lowering of viscosity. The viscosity effect usually requires the addition of another solvent such as aromatic naphtha or diesel fuel. Several possible reasons for this effect can be postulated. Skye Chem AD may act to stabilize asphaltenes and prevent them from forming large Nano-aggregates. Skye Chem AD may improve the size of the solvation sphere surrounding asphaltene micelles, lowering the interaction between the micelles, and preventing further agglomeration. Another possible effect is that Skye Chem AD may partially neutralize the effect of electrostatic condensation.

Effects of Skye Chem Products on Refinery Operations

The Skye Petroleum products used for sludge removal from oil storage facilities have all been examined for their potential effects on refinery operations. The elemental composition of Skye Chem WD and AD are given below:

Element	Skye Chem WD	Skye Chem AD
Carbon	84	82
Hydrogen	9.7	10
Oxygen	5	4.3
Nitrogen	0.512	1.6
Sulfur	1.57	1.9
Sodium	0.2	0

No Skye Chem product contains halogenated hydrocarbons or heavy metals. When applied at the typical use concentrations of 500 – 1000 ppm, the products contribute very little in the form of acids or other undesirable materials.

Chemical Selection

The choice of which Skye Chem product to use depends on the composition of the sludge, the available types of diluents, and the requirement to heat the mixture. Some examples are given below:

Sludge	Diluent	Recommended Products
Waxy sludge	Waxy crude oil	Skye Chem WD, Skye Chem X-110
Waxy Sludge	VMP Naphtha	Skye Chem WD
Waxy sludge	Varsol	Skye Chem WD, Skye Chem X-110, or X126
Waxy sludge with asphaltenes	Condensate	Don't do this EVER
Waxy sludge with asphaltenes	Diesel Fuel	Skye Chem WD, Skye Chem AD
Waxy Sludge with high asphaltenes	Diesel fuel	Skye Chem AD, Skye Chem WD, X110 or X126
Asphaltic sludge	Diesel Fuel	Skye Chem® AD
Asphaltic sludge	Crude oil and Xylene	Skye Chem WD

Recommendations Explained:

Waxy Sludge and Waxy Crude Oil Diluent

In this case we recommended a combination of Skye Chem WD and Skye ChemX-110. This is a combination of wax dispersant - Skye Chem WD, and a wax inhibitor - Skye ChemX-110. The dispersant is required to improve the penetration of the deposit and suspend the majority of the solids. The inhibitor works to prevent the recrystallization of the wax from the crude oil diluent.

Waxy sludge and a Non-waxy crude oil diluent

In this case only Skye Chem WD is required, unless the level of wax becomes too high for the oil to support the amount of wax dissolved.

Waxy Sludge with VM&P Naphtha as diluent

VM&P naphtha (or similar low boiling aliphatic solvents and condensates) is a powerful solvent for waxes and typically will not require more than a dispersant such as Skye Chem WD to remove a waxy deposit. However, these solvents will cause the precipitation of asphaltenes and should be avoided if any asphaltenes are present in the deposit.

Waxy Sludge with Varsol (or other refined light cycle oil)

This combination uses an intermediate boiling aliphatic refined product, such as light cycle oil, diesel fuel or varsol, with a waxy sludge, and will often only require Skye Chem WD to act both as dispersant and a pour point depressant. The combination of a middle distillate solvent and Skye Chem WD will also tolerate a fair range of asphaltenes before requiring other chemistry to be added.

Waxy sludge with low, intermediate and high asphaltenes with diesel fuel

This range of sludge is actually the most common. The combination of this sludge with a light cycle oil or similar refined product will only work if an asphaltene dispersant is added. Skye Chem WD is often required to penetrate the deposit, a wax inhibitor such as Skye Chem X-110 is required to control the pour point of the mixture and an asphaltene dispersant such as Skye Chem AD may be required to disperse and suspend the asphaltenes. Without the asphaltene dispersant an insoluble organic deposit will be created by the precipitation of the asphaltene fraction.

The more asphaltenes present in the mix the more asphaltene dispersant is required.

Asphaltic deposits with aliphatic solvents

While normally, we would not recommend an intermediate boiling range aliphatic solvent to dissolve an asphaltic deposit, we have found that the combination of such a solvent with Skye Chem AD has given the best results for the removal and dispersion of such deposits. In some laboratory tests, the combination of Skye Chem AD with this type of solvent gave better results than are found using an aromatic solvent. The addition of small amounts of an aliphatic solvent with Skye Chem AD to heavy crude has also been found to improve the ability of the oil to act as a solvent toward heavy asphaltic sludge.

The combinations are endless. In most cases the best way to determine the most effective combination is to test it in a laboratory.

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[i] Asphaltenes are by definition the fraction of crude oil that is precipitated by pentane.

[3] J.G. Speight " The Structure of Petroleum Asphaltenes – Current Concepts" Information series 81 Alberta Research Council 1978

[4] Dickie, J.P. and Yen T.F. "Marcostructures of Asphaltic Fractions by Various Instrumental Methods" Anal. Chem. 1967 39,p1847