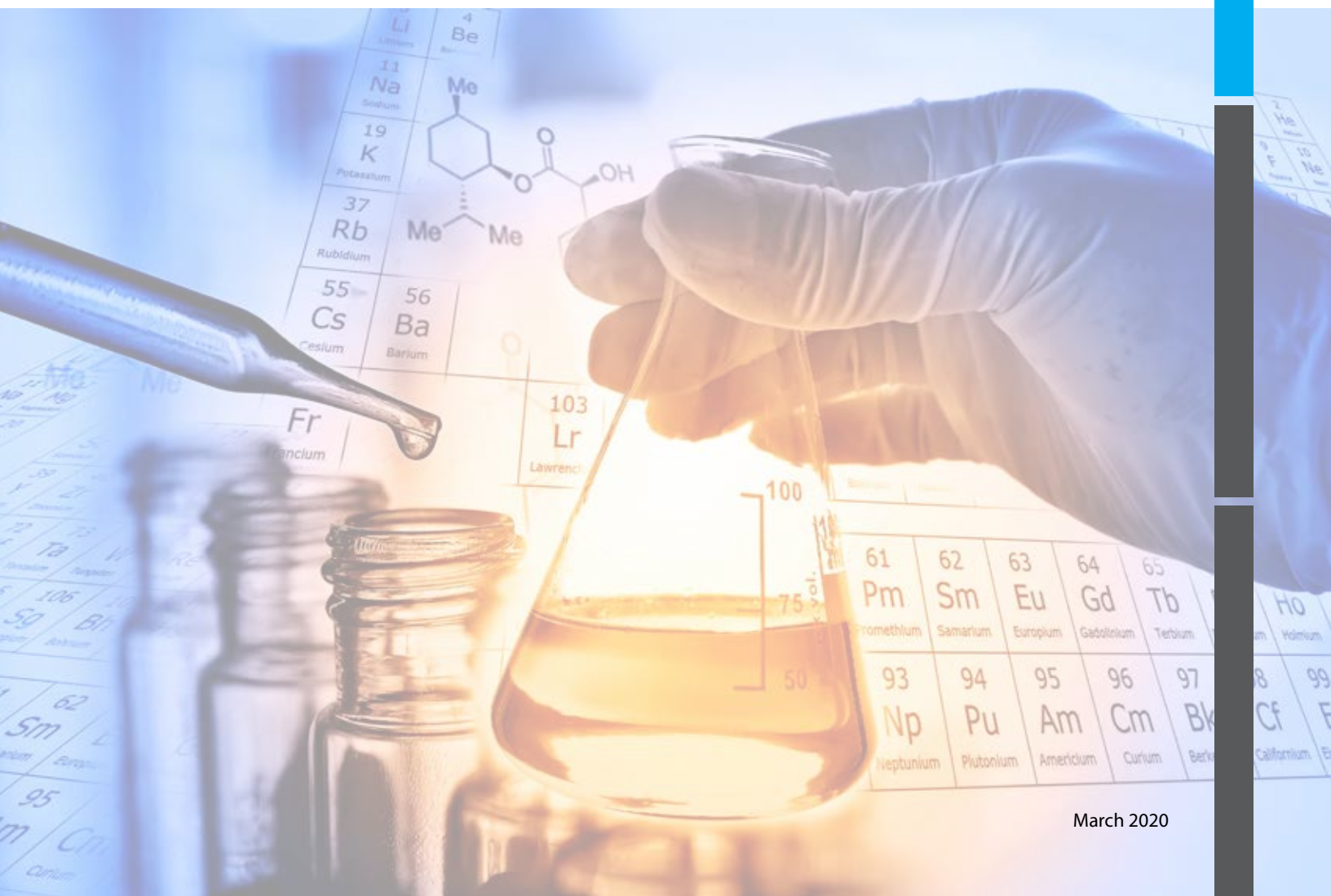


petroleum

technologies group L.L.C.

Determining Water in Oil Basics of Oil



Introduction

Contamination in oil-wetted systems from the early 90s has been proven to be responsible for up to 60% of all failures, especially in hydraulic systems. Since then more and more companies have spent time reviewing the design and operational procedures with the desire to reduce the failures relating to these failures. Contamination levels have fallen due to the efforts of these companies and because of this the reliability of equipment has drastically improved. Now days more emphasis is being put on overall cleanliness controls for the fluid systems in place.

Water can be found in oil generally in three different states:

A. **Dissolved (Minor Level)**

Small quantities of water will always be bound up in oil at the molecular level and the oil usually has a clear appearance, if it is not too oxidized. The amount of water that can be dissolved in the oil will depend upon the type of base stock used, its condition, its additive package and the temperature. The point at which oil cannot hold any more water is called the saturation point, and it is temperature dependent. For instance, a new, highly refined paraffinic circulation oil with few additives will hold little water before becoming saturated. At the other extreme, oils sometimes used in ship-board hydraulic systems or those used in rolling mill applications can have saturation levels quite higher. This is because they must keep relatively large amounts of water in suspension before allowing free water to coalesce and form large droplets. Synthetic oils have a natural tendency to hold water due to their chemistry depending on type.

B. **Emulsified (Major Level)**

When free water is present and the oil is subjected to a shearing action as occurs in pumps, gears and control valves etc., the water is broken down into small relatively stable droplets and these can be held in suspension; oils used in applications where water abounds, are formulated to promote emulsification rather than separation. In this state the water will affect the properties of the oil and hence the wear rates will increase but the water will not have a significant effect on the system corrosion rates.

C. **Free Water (Overloaded Level)**

Free water occurs when the oil can no longer hold any more water and it comes out of the oil as microscopic droplets and the oil can become hazy at this stage. Generally, any further increase in water content or decrease in temperature will cause more water to come out of the oil. These droplets can coalesce together to form larger droplets. If the relative density of the oil is <1.0 and the oil is stationary, the water will fall out of the oil due to gravity, generally into dead spots such as casings.

I. Effects of Water in Oils

The presence of water in the oil can have a wide range of effects, which include:

- A. Reduced lube film thickness
- B. Loss of lubricity
- C. Increased compressibility
- D. Fluid oxidation
- E. Additive depletion
- F. Accelerated surface fatigue
- G. Corrosion of component surfaces
- H. Icing at low temperatures
- I. Bacterial growth

Some of these are major and some are minor, but it is the authors' opinion that the greatest effect of water on the oil is to reduce the properties of the oil particularly its ability to lubricate and protect the component.

Damages to the components surfaces through increased wear, and the effects are triple edged:

- The presence of water accelerates the decomposition rate of the oil through Oxidization, especially when particles are present. The presence of reactive particles like iron and copper in combination with water greatly increases the degradation rate.
- Water in the oil reduces the lubrication film and exposes the moving surfaces to increased wear through abrasion, adhesion and fatigue.
- The presence of free water increases the compressibility of the oil in the contact zone of surfaces which further increases the wear rates and leads to a regenerative wear situation.

A factor that is often overlooked is that the acidic products are polar and have a high affinity for water. They readily dissociate from the oil to the water phase making the water more acidic and thus accelerate system corrosion rates.

II. Common Tests Performed to Determine Water Levelsⁱ

Visual Crackle Test

The simplest way to determine the presence of water in oil is to use the Visual Crackle test. While this is an effective test for identifying free and emulsified water down to say 500 ppm, its biggest limitation is that the test is nonquantitative and fairly subjective. False positives are possible with entrained volatile solvents and gases. Nevertheless, as a screening tool in the lab and the field, the crackle test will always have a role to play where a quick yes or no answer is required for free and emulsified water.



FTIR Analysis

FTIR can be an effective method for screening samples containing in excess of 1,000 ppm of water, provided a correct new oil baseline is available for spectral subtraction. However, due to its limited precision and comparatively high detection limits, FTIR is not adequate in many situations where precise water concentrations below **1,000 ppm or 0.1 percent** are required.

Karl Fischer

The Karl Fischer Moisture test is the method of choice when accuracy and precision are required in determining the amount of free, dissolved and emulsified water in an oil sample. However, even within the scope of Karl Fischer testing, there are several methodologies that are used. All Karl Fischer procedures work in essentially the same way. The oil sample is titrated with a standard Karl Fischer reagent until an end-point is reached. The difference in test methods is based on the amount of sample used for the test and the method used to determine the titration end-point. The most frequently used Karl Fischer method follows ASTM D1744 and involves volumetric titration of the sample, using a potentiometric cell to determine the end-point. While this method is reliable and precise, there can be reproducibility problems at low water concentrations (200 ppm or less). In addition, the test can be subject to interferences from sulfurous additives (for instance, AW and EP type additives) and ferric salts which may be present due to wear debris. Both of these react with the Karl Fischer reagent as if they were water and can give a false positive, resulting in an overstating of the water concentration. In fact, a new, clean, dry AW or EP oil may give a reading of as much as 200 to 300 ppm, due to the reaction of the additives, rather than because of excess moisture. More recently, labs have been switching to a coulometric titration method described in ASTM D6304. This method is more reliable than D1744 at low water concentrations and is less prone to interference effects, although again, AW and EP additized oils can show as much as 100 ppm of water as a result of the effects of the sulfurous additives. The most reliable method is ASTM D6304, complete with codistillation. With the codistillation method, the oil sample is heated under a vacuum so that any water present in the sample evaporates. The water vapors are condensed and dissolved into toluene, which is then titrated using the D6304 procedure. Because the additives and other interfering contaminants that may be present in a used oil sample remain dissolved or suspended in the oil, the condensed water in the toluene is free from interference effects and is a true count of water present in the sample. Another less commonly used method is ASTM D1533, which is used for determining water concentrations **down to 10 ppm or less** in transformer oils using a coulometric Karl Fischer reagent.

Other Methods

Saturation Meters, Calcium Hydride Test, Dean and Stark Method.

