

# Oil and Water Shouldn't Mix: Restoration of Steam Turbine Oil Demulsibility

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## Abstract

Steam turbines are responsible for up to 80% of global electricity production. Because steam powers these units, ingress of water into steam turbine oils is a common concern. As the saying goes: "Oil and water don't mix." When they do, failures and costly downtime may result. A lubricant's ability to separate from water is, therefore, paramount to the generating unit's reliability.

While turbine oils are engineered to readily separate from water, their ability to do so (demulsibility) often becomes impaired during service. The factors which impact demulsibility are many; fortunately, the solution to this problem remains the same regardless of its root cause. Indeed, well-engineered ion exchange-based treatment systems have shown considerable promise when it comes to the restoration of turbine oil-water separability. In addition to restoring demulsibility, these resins also allow for the removal of oil breakdown products (varnish etc.) which present a further challenge to power generators.

## Keywords:

Steam Turbine Demulsibility, Oil-Water Separation, Ion Exchange Treatment

## 1 INTRODUCTION

Turbines convert rotational energy into useful work using a shaft which sits in a bearing and are responsible for nearly all of the world's power generation. Lubricants are critical in these applications as they provide hydrodynamic lift to separate the shaft and bearing, allowing for the required rotation. In large industrial turbines, this shaft may weigh up to 100 tons and rotate up to 3,600 times per minute on a layer of oil only 0.02 – 0.1 mm thick [1] (Figure 1). Obviously the turbine oil in-service must be up to the task of supporting the shaft's load while facilitating its rotation.

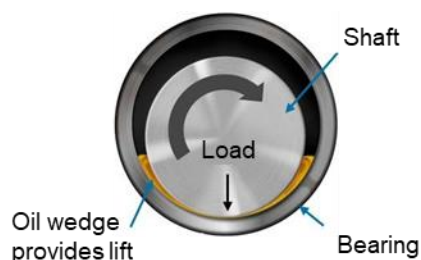


Figure 1 : Typical Steam Turbine Bearing Arrangement.

Although many turbine types are used to produce electricity, the vast majority are driven by steam [2]. As a consequence, steam turbine oils are often contaminated with water. This contamination may be the result of seal leakage, cooler failures, poor maintenance practices or atmospheric moisture ingress [3]. Regardless of how water enters an oil, its potential to cause harm is significant since it does not possess the properties required to keep the turbine's shaft and bearing apart.

In the power generation industry, the costs associated with failure and downtime are extremely high. It is, therefore, imperative to keep contaminant water away from critical lubricated components.

## 2 CONTAMINANT WATER IN STEAM TURBINE OILS

### 2.1 Free Water: Oil and Water Don't Mix

"Oil and water don't mix." This chemical observation is so universal that it forms the basis for a colloquialism which describes different personalities. While oil and water do not clash in the same way that people do, their basic chemistry ensures that they tend to remain separate from one another.

Like a bar magnet which has opposite poles, water is a polar molecule which features some positive charge on one end and some negative charge on the other (Figure 2a). This means that water molecules tend to pack together well, with one molecule's positive end attracted to an adjoining molecule's negative end. Indeed, these attractive forces are difficult to overcome and are responsible for many of the fluid's bulk properties.

The API Group I, II, III and IV base oils used in most lubricants, by contrast, are made up of non-polar hydrocarbon molecules with little to no separation of charge in any one part (Figure 2b). Such molecules are also subject to attractive intermolecular forces, however, these tend to be much weaker than those present in polar molecules like water.

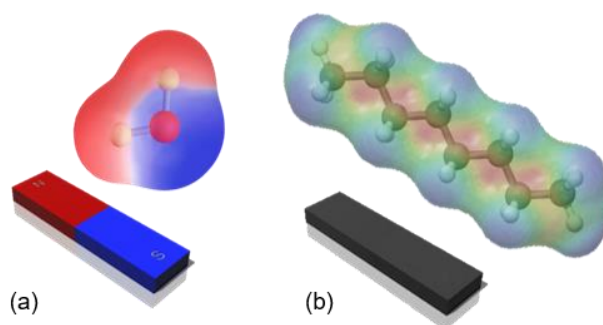


Figure 2 : Polarity of (a) Water and (b) a Hydrocarbon.

Because of their disparate polarities, oil and water are immiscible. Indeed, oils are generally referred to as being hydrophobic. When mixed, hydrocarbon-based oils and water rapidly separate. With no positive or negative ends, non-polar hydrocarbons are unable to overcome the favourable interactions that attract adjacent water molecules to one another, providing a thermodynamic justification for their hydrophobicity [4]. Once separated, the lighter density of oil leads to the formation of a layer which sits atop the denser water. Lubrication professionals typically refer to the lower layer as “free water.”

Free water can be extremely harmful in steam turbine applications. It may find its way to the shaft/bearing where it does not possess the load-carrying or lubricating abilities required to keep them apart. Clearly this is a situation operators wish to avoid. Fortunately, the ease with which water and oil separate generally allows for engineered solutions to prevent water from making its way to critical turbine components. Systems which employ gravity or centrifugal separation are common examples. Oil intake lines are also, generally, placed away from reservoir bottoms where free water is known to accumulate.

### 2.2 Dissolved Water: Oil and Water do Mix (a Little)

Despite their immiscibility, turbine oils, nevertheless, possess a finite ability to dissolve water. The solubility of water in a turbine oil varies as a function of operating temperature, however, water concentrations of up to 100 ppm are frequently accommodated under typical conditions [5]. At such low moisture levels, the likelihood of one water molecule attracting another is small and they, therefore, tend to be statistically dispersed among the far more prevalent oil molecules.

In this dissolved state, water has little impact on the fluid’s bulk lubrication properties and the immediate risk to equipment is relatively minor. Dissolved water can, however, promote chemical breakdown of the turbine oil and its additives. It may also promote corrosion within equipment. Efforts should, therefore, be made to keep turbine oils as dry as is reasonably possible.

### 2.3 Emulsions: When Oil and Water do not Separate

Without agitation, water in turbine oils tends to exist in either a free or dissolved state. During service, however, oils are often agitated as they move through a lubricating system. If free water is present, this agitation promotes the formation of water in oil emulsions. These emulsions feature a fine dispersion of water droplets suspended within the turbine oil. Emulsions are readily identified by their “cloudy” or “milky” appearance which is the result of light scattering as it passes through the many oil-water interfaces present. The term itself is even derived from the Latin for “milk” (which itself is an emulsion of fat in water).

In new oils and oils in good condition, emulsions are unstable and oil and water quickly revert to their, more thermodynamically stable, separate states. As turbine oils breakdown or become contaminated during service, however, the accumulation of surface-active agents can kinetically stabilize emulsions. Although the exact physics of emulsion-stabilization are complex, it is generally accepted that polar oil contaminants will stabilize emulsions formed with water (which is also polar). These polar contaminants allow the lubricant to more favourably interact with water. They also interfere with the attractive forces that promote free water agglomeration. In turbine applications, an emulsion is said to be “persistent” if it

does not readily separate into its constituent oil and water layers in 30 minutes or less.

Persistent (or stable) emulsions have the potential to be extremely harmful in lubricant applications since their physical properties are not sufficient to effectively lubricate equipment components. In steam turbines, an emulsion cannot provide the required hydrodynamic lubrication at the bearing. Making matters worse, the water present in an emulsion promotes bearing corrosion and wear.

While steam turbines feature engineered solutions to prevent free water from reaching the bearing, these rely on the efficient separation of oil and water. In the case of stable emulsions, these engineered solutions do not effectively prevent water from reaching the bearing or other critical equipment components.

## 3 DEMULSIBILITY TESTING

Given that steam turbines rely upon the efficient separation of contaminant water in their lubricating systems, it is imperative to monitor their oil-water separation abilities (often called demulsibilities). To this end, ASTM D1401 has been generally adopted as an industry-standard test for turbine oil demulsibility [6].

The demulsibility test mixes 40 mL of oil with 40 mL of water for 5 minutes under reproducible conditions. Once the mixing period is complete, the separation of the oil-water mixture is monitored. Every 5 minutes, the volume of oil, volume of water and volume of emulsion present are recorded. Once there is less than 3 mL of emulsion present, the test is stopped and the final result is reported as: “mL oil-mL water-mL emulsion.” The time that was required to complete the test is also recorded in brackets following the component volumes. For example, a 40-40-0 (5) result indicates that, 5 minutes after mixing stopped, the 40 mL oil and 40 mL water present completely separated and that no emulsion remained (Figure 3a); this is a perfect result and indicates that the oil had excellent water separation abilities. When a sample has been allowed to separate for 30 minutes but more than 3 mL of emulsion remains, the test is also stopped and the result is reported as above. For example, a 25-20-35 (>30) result indicates that there was still 35 mL of emulsion present (in addition to 25 mL oil and 20 mL water) 30 minutes after mixing stopped (Figure 3b). The emulsion in this latter example is said to be persistent or stable.

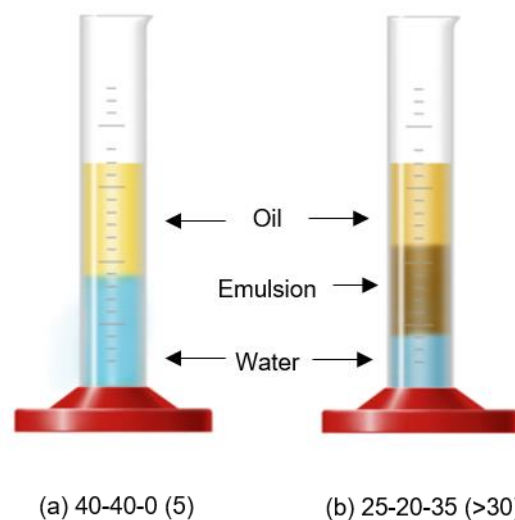


Figure 3 : Example Demulsibility Test Measurements.

#### 4 EFFECT OF POLAR CONTAMINANTS ON TURBINE OIL DEMULSIBILITY

There is extensive anecdotal evidence to suggest that oil breakdown products and polar contaminants have a detrimental impact on steam turbine oil demulsibility. With the aim of conclusively demonstrating their effect, we, therefore investigated the impact that organic acids had upon the water separation ability of a common Group II turbine oil.

In-service the oxidative production of organic acids, like the formic and oleic acids tested, is well-established in turbine oils. Formic acid (pKa = 3.74) is a more polar acid while oleic acid (pKa = 9.85) is a less polar acid. Virgin oil was selected for this experiment to eliminate the potential impact that depleted additive levels and other contaminants might exert upon demulsibility. This virgin sample was spiked with formic or oleic acid to produce test samples whose acid numbers (ANs) were approximately 0.2 and 0.4 mg KOH/g higher than that of the virgin lubricant. The demulsibilities of these samples are summarized in Table 1.

Fluid	Acid Number (mg KOH/g)	Demulsibility	Separation Time (minutes)
Virgin	0.12	40-40-0	13
Virgin + Oleic Acid	0.39	40-40-0	18
Virgin + Formic Acid	0.39	40-40-0	15
Virgin + Oleic Acid	0.56	40-40-0	20
Virgin + Formic Acid	0.53	30-40-10	> 30

Table 1 : Impact of Contaminant Organic Acids upon Turbine Oil Demulsibility.

The obtained results confirm that organic acids have a detrimental impact on the water separation abilities of turbine oils. While the virgin oil separated completely from water in 13 minutes, all of the acidified samples required more time to do so. Acid concentration also exerted an influence on the required oil-water separation time with more acidic samples requiring more time to separate. Finally, the polarity of the acid influenced water separability as evidenced by the much poorer demulsibility of the 0.53 mg KOH/g formic acid sample (30-40-10 (>30)) relative to that of the 0.56 mg KOH/g oleic acid sample (40-40-0 (20)). At higher concentrations, the more polar formic acid-spiked oil was the only sample which yielded a stable emulsion. The fact that high levels of less-polar oleic acid did not produce persistent emulsions is somewhat remarkable and demonstrates the key role that polarity plays in stabilizing oil-water emulsions.

Many other polar turbine oil contaminants are likely to exert a similar influence on oil-water separability, however, their systematic investigation was beyond the scope of our present study.

#### 5 DEMULSIBILITY RESTORATION

##### 5.1 Demulsibility Improvement via Top-Up with Alternative Lubricants or Additives

###### *Top-Up with Alternative Lubricants*

A recent EPRI paper highlighted several case studies wherein the addition of Group I makeup oil to Group II reservoirs had a beneficial impact on the oil mixtures' water separation abilities [7]. We note, however, that a more controlled laboratory study also outlined in the same report revealed that not all Group I oils performed well in this regard. Indeed, the addition of 1 type of Group I oil was found to have a beneficial impact while the addition of another proved much less effective. As a result, the observed demulsibility improvements were determined to be due to additives present in the make-up oils and not the base fluids themselves. Such improvements might well have occurred following the addition of a well-selected Group II product.

While some promising results were achieved in the 3 case studies described, the Group I sweetening approach is risky in that the oils to be mixed cannot be guaranteed to be compatible. For this reason, detailed testing must be completed prior to Group I addition and, even this, cannot entirely prevent unforeseen interactions during oil service. This approach complicates oil chemistry, making outcomes more difficult to predict. The study even notes that "oil suppliers recommend against these mixtures, due to the unpredictable nature of oil interactions." Indeed, the impact of sweetening on vital parameters such as oxidative stability and additive lifetime was not addressed in EPRI's report.

###### *Top-Up with Aftermarket Additives*

Another recent study examined the impact that an aftermarket polar additive (Boost VR) had upon in-service oil demulsibility [8]. The study's authors claim that the additive enhances oil solubility which "may correct water separation characteristics." Unfortunately, the data that they present fails to support this conclusion. In the 18 trials that the authors conducted, only 6 of the fluids' demulsibilities improved while 9 remained unchanged. Most notably, 3 of the lubricants' water separation abilities worsened following the addition of Boost VR. A closer examination of the study's data reveals that Boost addition actually led to a slight increase in the average amount of time required for oil-water separation.

While the addition of foreign products to turbine oil reservoirs may, in some cases, improve oil-water separability, this approach is too unpredictable and risky to merit widespread use. It also suffers from the disadvantage that the make-up oil/additive tends to be an inherently less-stable product which itself is prone to further breakdown. The addition of any foreign product to an oil complicates the fluid's chemistry, increasing the risk of unforeseen consequences.

##### 5.2 Demulsibility Improvement via Treatment with Ion Exchange Resin

While oil-sweetening complicates the chemistry of lubricating systems, an alternative approach simplifies it via the use of well-engineered ion exchange resins. These products rely on adsorption and have now been used to effectively remove polar breakdown products and contaminants from turbine oils for many years [9].

As engineered products, the chemistry of ion exchange resins can be precisely controlled to ensure that no contaminants are unintentionally added during treatment. Alternative natural products like Fuller's Earth, clays and zeolites cannot make this claim. Moreover, ion exchange resins can be tailored to selectively remove undesirable

polar contaminants without adversely impacting the level of polar additives in turbine oils. By removing contamination, ion exchange resins simplify oil chemistry, restoring it to a "like-new oil" state. As a result, ion exchange-treated oils often separate from water like they did prior to being put in-service.

#### *Demulsibility Restoration via Lab-Scale Ion Exchange Treatment*

With the aim of demonstrating how ion exchange resins can be used to restore lost turbine oil demulsibility, we subjected 14 different in-service steam turbine oils to lab-scale treatment with proprietary ICB™ ion exchange products. Small (150 - 250 mL) reservoirs of the oils were treated via kidney loop-type filtration through the ion exchange media. The process used is, essentially, a lab-scale version of commercially available Soluble Varnish Removal (SVR™) systems. The water separation results from these 14 trials are summarized in Table 2.

Prior to ion exchange treatment, 10 of the 14 oils tested produced stable emulsions and were, therefore, unfit for continued service. In some cases, emulsion accounted for over 90% of the fluid volume even 30 minutes after mixing. Alarming, each of these steam turbine oils was actually in-service at a real-world generating facility.

Fortunately, ion exchange treatment of these oils led to significant improvements in their water separation abilities. Indeed, 13 of the 14 oils tested (93%) featured acceptable or nearly acceptable demulsibility values following lab-scale treatment. This is a marked improvement given that only 4 of these lubricants (29%) were in similarly good condition initially. We note that the 1 oil which failed to produce an acceptable post-treatment demulsibility featured an extremely poor 0-11-69 (>30) value initially. It is likely that this oil was simply too badly degraded to restore.

Ion exchange treatment also yielded oils with significantly lower tendencies towards emulsion formation. Indeed, the treated fluids produced an average of 35% less emulsion than their pre-ion exchange analogs. In the most remarkable case, ion exchange treatment decreased the volume of emulsion present by 89% (from 75 mL to 4 mL).

Finally, the use of ion exchange also allowed the oils to separate from water more quickly with the treated fluids requiring an average of 31% less time to reach the ≤ 3 mL emulsion mark. This improvement is particularly significant since it ensures that the reservoir residence time of treated turbine oils will be sufficient to allow for free water separation. Once separated, existing engineering measures then allow for the moisture's removal, mitigating the risks associated with water ingress.

These results highlight the potential effectiveness of ion exchange as a treatment strategy for turbine oil demulsibility restoration. Indeed, the water separability of each of the 14 in-service sample oils improved as the result of ICB™ treatment. This is in contrast to the strategy of sweetening with lower-quality Group I oils which yielded mixed results and an elevated risk of incompatibility. As an additional benefit, the ICB™ resin also removed turbine oil varnish and its precursors (acids and oxidation products). During lab-scale trials, the acid numbers, FTIR oxidation levels and MPC varnish potentials of the treated lubricants fell by an average of 48%, 43% and 64%, respectively. The improved demulsibilities noted in this investigation are likely a direct result of the removal of these polar contaminants.

The obtained results demonstrate why operators should seek to simplify their oil chemistry rather than making it more complex.

<b>In-Service Oil Sample</b>	<b>Initial Demulsibility</b>	<b>Post ICB™ Demulsibility</b>	<b>Demulsibility Improvement</b>	<b>Emulsion Decrease (%)</b>	<b>Separation Time Improvement (%)</b>
1	40-25-15 (>30)	40-40-0 (10)	0-15-15 (20)	19	67
2	39-8-33 (>30)	40-36-4 (>30)	1-28-29 (0)	36	0
3	5-0-75 (>30)	40-36-4 (>30)	35-36-71 (0)	89	0
4	40-33-7 (>30)	40-40-0 (10)	0-7-7 (20)	9	67
5	5-24-51 (>30)	46-34-0 (>30)	41-10-51 (0)	64	0
6	15-25-40 (>30)	41-38-1 (15)	26-13-39 (15)	49	50
7	40-37-3 (30)	40-38-2 (10)	0-1-1 (20)	1	67
8	0-27-53 (>30)	41-37-2 (25)	41-10-51 (5)	64	17
9	0-11-69 (>30)	9-22-49 (>30)	9-11-20 (0)	25	0
10	40-38-2 (15)	41-39-0 (10)	0-1-2 (5)	3	33
11	4-3-73 (>30)	37-37-6 (>30)	33-34-67 (0)	84	0
12	40-38-2 (15)	40-38-2 (10)	0-0-0 (5)	0	33
13	40-38-2 (10)	40-38-2 (5)	0-0-0 (5)	0	50
14	30-18-32 (>30)	40-40-0 (10)	10-22-32 (20)	40	67
<b>Average</b>	<b>24-23-33 (26)</b>	<b>38-37-5 (18)</b>	<b>14-14-28 (8)</b>	<b>35</b>	<b>31</b>

Table 2 : Demulsibility Improvements due to Lab-Scale Ion Exchange Treatment of In-Service Steam Turbine Oils.

### Case Study: On-Site Demulsibility Restoration via Ion Exchange Treatment

In 2016, operators at a 759 MW coal-fired power plant expressed concern about the failing demulsibility of one of their steam turbine oils. Following a lab-scale demonstration similar to those above, the end user installed an ICB™ ion exchange treatment system. Over the course of several months, the generating unit was treated with ion exchange resin and no new make-up oil was added to the system. As anticipated, the oil's tendency towards emulsion-formation fell by a dramatic 94% while the time required for oil-water separation decreased by more than 20 minutes. Following the treatment period, operators no longer had cause for concern as the demulsibility of their turbine oil improved from 32-16-32 (>30) to 39-39-2 (10) (Table 3). Clearly, improvements resulting from lab-scale trials are scalable, making ion exchange treatment an excellent option for on-site demulsibility restoration.

Sample	Demulsibility	Acid Number (mg KOH/g)	MPC ΔE	FTIR Oxidation (%)
Pre-ICB™	32-16-32 (>30)	0.08	5.5	45
Post-ICB™	39-39-2 (10)	0.06	3.9	28

Table 3: Oil Condition Improvements due to On-Site Ion Exchange Treatment at a 759 MW Power Plant.

## 6 SUMMARY

Steam turbines are responsible for up to 80% of global electricity generation, however, their performance and reliability depends on a layer of turbine oil which is less than 0.1 mm thick. Since this lubricant must support the turbine's shaft, it is imperative that it possesses the load-bearing and lubricating abilities required to do so.

The steam which powers these units often contaminates turbine oils, impairing their ability to lubricate critical components. This moisture also leads to corrosion and decreased oil lifetimes. At very low levels, turbine oils can accommodate this water, keeping it in a dissolved state which does not impact lubrication. When water levels exceed approximately 100 ppm, however, the old adage "oil and water don't mix" becomes apparent as free water separates into its own distinct layer. This ready separation is key to reliability since steam turbines feature a variety of engineering measures designed to remove free water.

As oils break down during service, however, polar contaminants accumulate, increasing the fluids' propensities towards emulsion formation. The impact that polar contaminants have on demulsibility was conclusively demonstrated herein by spiking virgin turbine oil samples with organic acids similar to those which arise during service. Once emulsions form, it is essential that they revert to their more stable, separate oil/water phases

in a timely manner. Persistent emulsions are especially harmful as they do not possess the lubricating abilities required. Worse still, stable emulsions cannot be removed using the same general measures that are employed to address free water contamination.

Fortunately for power producers, several strategies exist for the restoration of turbine oil demulsibility. Recent studies highlighted the potential for using foreign lubricant or aftermarket additive make-up to this end. This strategy, however, complicates oil chemistry leading to a significant risk of incompatibilities over time.

Ion exchange resins represent an alternative strategy which, instead, seeks to simplify oil chemistry by removing polar contaminants. This strategy was shown to be highly effective during laboratory trials which showed that ion exchange-treated oils produced an average of 35% less emulsion than their untreated analogs. More importantly still, ion exchange treatment led to a 31% average decrease in the amount of time that emulsions required to separate into their constituent oil and free water layers.

In addition to proving effective on a lab-scale, ion exchange treatment was demonstrated to be scalable at a 759 MW power plant. By filtering their turbine oil through ion exchange resin, operators at this site were able to improve their lubricant's demulsibility from 32-16-32 (>30) to 39-39-2 (10). This improvement also allowed the turbine's users to remove varnish and other harmful contaminants from their fluid.

Oil and water should not mix. Fortunately, when they do, steam turbine operators are now equipped with the tools required to keep their generating units running in optimal condition.

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