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ASSESSING OXIDATION CONDITION AND LUBRICANT REFRESHMENT IN TURBINE OILS

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ABSTRACT

Turbines are critical pieces of equipment for power plants and related industries. Varnish formation is the first root cause for down time and loss of reliability in turbines. The lubricant's oxidation condition can be effectively monitored through RULER (Remaining Useful Life Evaluation Routine), MPC (Membrane Patch Colorimetry) and RPVOT (Rotating Pressure Vessel Oxidation Test) tests. Besides the nominal ASTM (American Society for Testing and Materials) value for these tests, significant information can be gathered from digging into these tests and integrating their outcomes. One major application for this integration is the estimation of the lubricant refreshment for lean operation. Through lab tests, this can be accurately estimated, by planning ahead of the upcoming maintenance intervention. This method will be shown, together with case studies.

INTRODUCTION

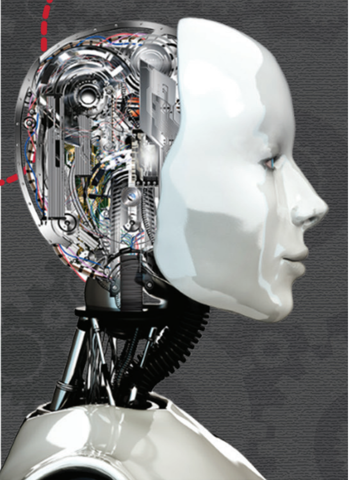
Turbines are critical pieces of equipment for power plants and heavy industries. They are expensive components that must operate reliably. In the case of heavy industry, downstream operation fully depends on their power generation. In the case of power plants, down time implies production loss and penalties for contract non-compliance.

In turbines, lubrication undergoes a hydrodynamic regimen in which wear arises only after very poor lubricant condition. Conversely, the main root cause of turbine failure is the formation of deposits. Deposits produce several detrimental effects of these systems, such as sticking valves, orifice obstruction and inefficient heat exchange. Also, deposits can have different natures (i.e.: inorganic, organic, biological) (Wooton & Livingstone, 2013).

In the case of gas turbines, where the lubricant suffers mainly from thermal stress, deposits are usually associated with the formation of varnish. Varnish is commonly associated with oxidation processes. It is composed of sacrificed antioxidants and oxidation products that coalesce to form sticky soft matter. The cost of varnish is very high both in downtime and in equipment replacement. For this reason, monitoring of the oxidation condition of turbine oils is of utter importance.

To prevent the base oil from oxidation, turbine lubricants are supplemented with about 1% of antioxidants. These are sacrificed to protect the base oil from free radicals and thermal and oxidative stress. It is usually accepted that turbine oils can be used until their remaining active antioxidants are 25% of the original formulation. In many cases, however, depending on the oil, varnish issues arise much before this point. Both laboratory tests (Yano et al, 2004) and turbine oil condition monitoring, show that varnish may start to build up even when remaining antioxidants are as high as 60%.

In order to keep the operation reliable, the oxidation condition of a turbine must be kept between safe boundaries. This implies keeping a high dose of antioxidants, and the varnish potential low, to predict a high oxidation resistance. Oil refreshment is a viable option to keep turbines free of varnish. By integrating the outcomes of lubricant analytics, such as RULER, RPVOT and MPC, it is possible to estimate the refreshment required to keep the turbine under lean operation.



MPC, RPVOT AND RULER ARE COMPLEMENTARY TESTS IN OXIDATION CONDITION MONITORING.

MPC

Membrane Patch Colorimetry (MPC) (ASTM D7843) is a method for determining varnish formation in mineral turbine oils. In analytical chemistry, procedures can be classified as either end point or standardised. Typical end-point procedures are titrations such as Acid Number (ASTM D974) or Karl Fischer (ASTM D6304).

In these, the test ends with an end-point indicator, which can be colorimetric, potentiometric, amperometric, etc. Conversely MPC (ASTM D7843) is a standardised procedure.

In this procedure, the lubricant is heated at 60ºC for 24h, to mimic the turbine operation temperature and to redissolve varnish. After heating, the oil has to stand for 72 hours in the dark for varnish to re-precipitate. This is the critical standardised step, given that varnish precipitation increases with time. After filtering through a 0.45 µm-pore membrane, the colour of the patch is measured using the CIELAB colour space and the ΔE, that indicates intensity, is measured.

A higher ΔE (or MPC) indicates that more varnish has been retained by the membrane patch. Consensus is that an MPC > 30 is condemning, MPC > 20 is alarming and MPC < 15 is a safety zone.

To prove the criticality in the precipitation step, a sample was filtered after different precipitation times. Figure 1 shows MPC results for a sample after 72h precipitation; 168h precipitation; and four months after oil sampling (~3000h).

The results show the importance in keeping standardised times in order to have repetitive results which can be trended for adequate condition monitoring.

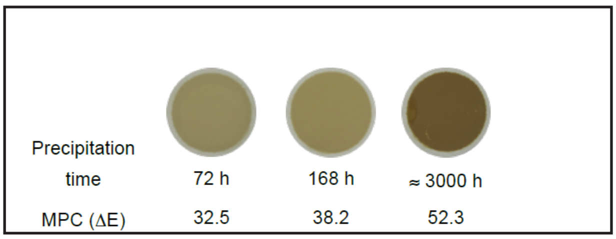


Figure 1. MPC is a standardised method in which precipitation time is critical (part I).

Turbine oil was heated to 60ºC for 24 hours and stood to precipitate for 72h; 168h or four months before filtering and determining the MPC value.

Results show that MPC significantly rises with longer precipitation times.

RPVOT

The Rotating Pressurised Vessel Oxidation Test (ASTM D2272) is an oxidation simulator. Briefly, a sample of lubricant is pressurised at 190psi under an oxygen atmosphere at 150°C and rotated in the presence of a copper catalyst and water vapour.

The time curve of the vessel pressure is recorded. During the test, the lubricant tends to oxidise due to the high oxygen potential. In the first stages of the test, antioxidants sacrifice themselves to protect the base oil and therefore oxygen pressure remains steady. Once antioxidants are fully depleted, the base oil starts bulk oxidation and oxygen pressure drops.

ASTM D2272 defines the induction period of a lubricant as the time until the pressure drops by 25.4psi.

Figure 2 shows the RPVOT curves for different lubricant formulations. In the case of turbine oils formulated with Group I base-stocks, the RPVOT curve remains steady until the antioxidants are depleted. It is usual to see intermediate inflection points showing titration of each antioxidant.

Once antioxidants are depleted, the base oil suffers massive bulk oxidation, and the pressure drops sharply. In the case of Group II base-stocks, RPVOT curves also present an initial steady phase during antioxidant protection, but later oxygen pressure declines in a gradual manner. This accounts for the enhanced resistance of hydro-treated base-stocks to oxidation.

However, this does not imply an enhanced resistance to varnish formation. Hydrotreated base-stocks are less polar than Group I base-stocks, and therefore varnish is usually less soluble in Group II base-stocks. Group III GTL base oil formulations have extraordinary long RPVOT, with steady induction periods and sharp endpoints.

Finally, Group V polyol-ester base aeroderivative turbine oils are interesting because the vessel remains pressurised at about 100psi, indicating formation of gaseous species as oxidation products. Also, in this case the endpoint of the test, according to ASTM D2272, falls far from the pressure drop.

From this, we learn that a lot of information is present in the complete RPVOT curve and therefore this test should not be stopped after a 25.4psi pressure drop but should be continued until the pressure drops by at least 90psi.

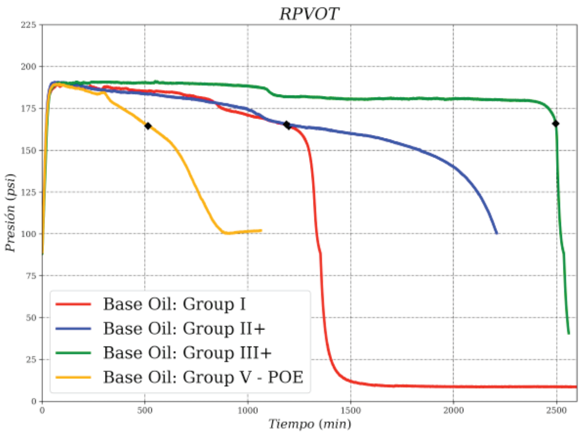


Figure 2: RPVOT curves for different base oil formulations.

Depending on the base oil and antioxidant formulation, lubricants have different RPVOT curves. The ASTM test was designed for Group I oil, in which the standard induction period (◊) coincides with oxidation of the bulk oil. So do Group III+ base oil formulations. In Group II+ base lubricants and Group V aeroderivative polyol-ester base lubricant, standard induction periods are far from the bulk oxidation. To test for this, RPVOT tests should be driven until a 100psi pressure drop is reached.

RULER

Ruler (ASTM D6971) is a voltammetric method for dosing antioxidants. Briefly, an oil aliquot is diluted in a vial which extracts the antioxidants and decants the base oil.

The sample is then probed under a potentiostat, with a linear increasing voltage applied. Each antioxidant, depending on its nature, is oxidised at a specific potential and an amperometric peak arises. In oils supplemented with aromatic amines and phenols, two peaks can be observed. The area under the curve for each peak is proportional to the antioxidant concentration.

The area of an in-service lubricant compared to that of its original formulation dictates each remaining antioxidant percentage in the in-service oil. An educated reading of the amperogram provides additional information on the health of the in-service oil. As the oil degrades, it is seen how the antioxidant peaks become shifted from their original potential.

RULER is an excellent methodology for monitoring the remaining active antioxidants. Given that the method actually oxidises the antioxidant, the result is trusty of the real remaining antioxidant potential. However, when the remaining antioxidants are very low and the peaks are very shallow it is possible to make errors in the antioxidant quantification, typically in excess.

Excess quantification in degraded samples is dangerous, because should antioxidants completely deplete, the lubricant will fall into massive oxidation in a very short period, causing huge damage. To avoid falling into this analytical pit, it is possible to better estimate the remaining antioxidant % by extrapolation.

When preparing mixtures of new and used oil, we can define the Refreshment % such that Refreshment = 0% implies used oil; and Refreshment = 100% implies full lubricant replacement.

$$Refreshment = \frac{New\ Oil}{New\ Oil + Used\ Oil} \cdot 100\ \%$$

Consider the following case study of a Gas Turbine with a mineral ISO VG 32 lubricant supplemented with an R&O package and 43,000 operation hours.

The RULER for this sample resulted in 28,3% remaining antioxidant, very close to the condemning limit. To better assess the RULER value, we proceeded to perform the extrapolation method. For this, the complementary mixtures of new and used oil to cover 0% to 100% refreshments were prepared. After thorough homogenisation, RULER was tested for all samples. Figure 3 shows the RULER outcome.

Given that the prepared samples are a mixture of new and used oil, the remaining antioxidant % has to be linear. However, if we plot these results (Figure 3b), we can see how the plain in-service oil (0%R) clearly falls out of the linear curve. Hence, the actual remaining antioxidant concentration in the in-service oil is 14,9% (yintercept) and not 28,3% as would have been estimated by the traditional RULER method.

Through RULER analysis, it is also possible to check the synergy between antioxidant chemistries. Turbines usually operate using a mixed antioxidant lubricant. This is a mixture of phenols and amines. Amines and phenols work synergistically in keeping the base oil healthy.

Amines are reactive antioxidants which rapidly take free radicals, protecting the base oils by terminating chain reactions which would otherwise degrade the base oil.

Hindered phenols, on the other hand, are slower reactants, but have the potential to regenerate the oxidised amines and become stable free radicals themselves (Fig. 4b). RULER analysis can demonstrate antioxidant interaction.

Consider a gas turbine lubricated with a Group I oil supplemented with a mixed antioxidant package. This system has run for 55,000 operating hours with a 10% refreshment after 44,000 operating hours.

Refreshment plots were performed for this lubricant.

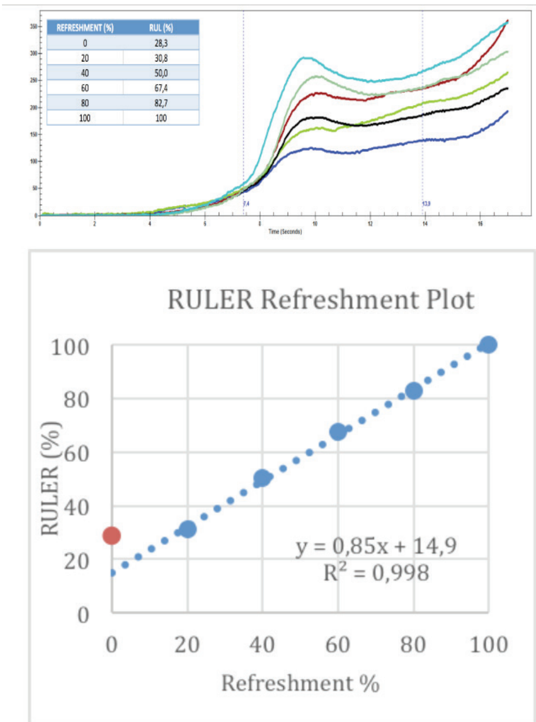


Figure 3. RULER can be quantified by extrapolation in degraded samples.

Panel (a) shows amperograms for refreshment samples of a Group I Turbine Oil together with their quantification. In panel (b), the data is plotted.

Original sample (0% refreshment) clearly falls off the linear plot.

Figure 4 shows the synergic effect of aminic and phenolic antioxidants. In the plain in-service oil, the phenolic antioxidant has completely depleted and the aminic antioxidant keeps 70% of the original formulation.

Figure 4 shows the synergic effect of aminic and phenolic antioxidants. In the plain in-service oil, the phenolic antioxidant has completely depleted and the aminic antioxidant keeps 70% of the original formulation. If antioxidants do not interact, the refreshment plots should be linear for each antioxidant, as is shown in the dotted lines. Instead, when a 40% Refreshment sample is analysed, it is observed how the aminic antioxidant recovers by excess to 93% and how the phenolic antioxidant recovers by defect, only to a 25%. During the preparation of the RULER test, the phenolic antioxidants have regenerated the aminic antioxidants almost to their full potential. This reaction is immediate compared to the turbine operation timescales.

We can also calculate the TOTAL ANTIOXIDANT % as the sum of the antioxidant areas in the in-service oil divided by the sum of the antioxidant areas in the fresh oil.

The reader and analyst should be aware that calculating the TOTAL ANTIOXIDANT % is different to the analytic named as TOTAL RUL in the RDMS software.

Most interestingly, the TOTAL ANTIOXIDANT % draws a perfect linear fit, a fact that correlates to the model. From the condition monitoring perspective, the fact that a lubricant keeps full synergy between antioxidants indicates that antioxidants have not oxidised irreversibly.

Should irreversible oxidation occur, it would be expected to find a high varnish load in the oil and in the lubricated surfaces of the gas turbine.Should irreversible oxidation occur, it would be expected to find a high varnish load in the oil and in the lubricated surfaces of the gas turbine.

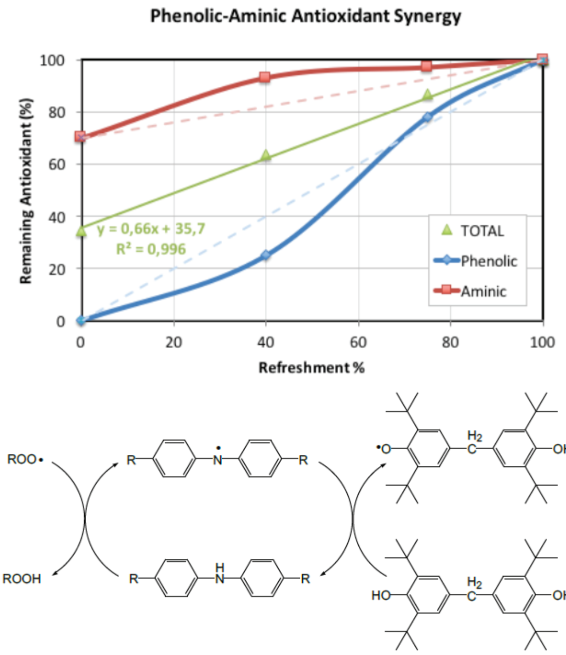


Figure 4. Refreshment plots are a useful tool to verify antioxidant synergy rbine oils.

(a) A turbine oil depleted of phenolic antioxidants was refreshed with new oil. The dotted lines indicate the theoretical behaviour without lubricant interaction. While the total antioxidant trace is linear, experimental data for aminic antioxidants are higher than the linear trace, and experimental data for the phenolic antioxidants are lower than the theoretical trace. This indicates that fresh phenols regenerate oxidised amines.

(b) Chemical reactions showing amine refreshment by fresh phenols. Figure extracted from Gatto et al, 2006 & 2007. See references.

BUILDING AN OXIDATION CONDITION MODEL FOR ESTIMATING LUBRICANT REFRESHMENT.

The motive for integrating oxidation condition analysis and performing refreshment plots is to plan lubricant refreshments for turbines. In order to build a model for lubricant refreshment, one must assess the different scenarios that exist between the actual condition of the turbine and a hypothetical situation resulting in a full lubricant change.

The study will be conducted on the gas turbine described in figures 1 and 3. This gas turbine is lubricated with a Group I - ISO VG 32 oil supplemented with aminic antioxidants. The lubricant has been in service for 43,000 hours.

For this analysis, the lab will need to work with one litre of in-service turbine oil plus one litre of the fresh oil. Analysing the in-service oil, we find the following data:

	In-service Oil	New Oil
RULER	14,9 %	100 %
RPVOT	142 min	1369 min
MPC	34	1

The oxidation condition of the lubricant is poor, and the lab was commissioned to undertake a project to analyse the oxidation condition and to propose a lubricant refreshment. At first, MPC and RPVOT tests were performed for 0% and 100% Refreshments.

As we have shown, RULER analytics of degraded samples can be quite uncertain, so full refreshment analysis was conducted, where the actual remaining antioxidant was 14.9%, instead.

The preliminary refreshment model is built with the MPC and RPVOT data of the in-service and new oils and the refreshment RULER data. The preliminary model makes a gross refreshment estimation for MPC and RPVOT refreshment simulation.

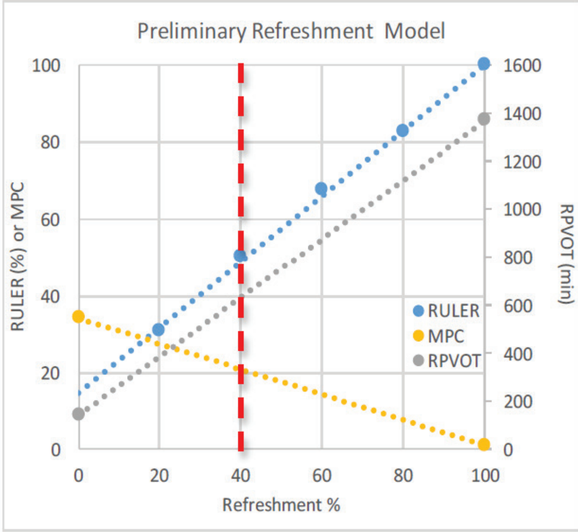


Figure 5. Preliminary model for turbine oil refreshment.

The preliminary model shows that antioxidants fall under the recommended 25%. RPVOT shows a similar trend, being for the in-service induction period - only 142min, and about 10% of the new oil. This value, in agreement with the RULER, is very low and may result in bulk oil oxidation in the short term.

Lastly, the MPC value of 34, has exceeded the alarm limit and is close to the condemning value. The preliminary conclusion is that the lubricant in this turbine is getting close to the end of its life cycle, however if a full change is not possible, refreshment can help the turbine run reliably in the midterm.

The desirable oxidation condition for the turbine to run lean should be:

- ANTIOXIDANT > 50%
- MPC ≈ 15
- RPVOT > 500 minutes

According to the preliminary model, this can be achieved if 40% of the lubricant is changed. In such a scenario, antioxidant rises to 50%; MPC is reduced to about 21 and RPVOT can be estimated in about 600 minutes. However, to have better confidence on the prediction, 40% Refreshment samples are prepared for RPVOT and MPC analysis. With this data, we can build the following iterated model presented in Figure 6.

The RPVOT value for the 40% refreshment is significantly higher than the expected RPVOT for the linear model.

This trend is seen in all refreshment studies. It is interesting to compare this trend with that of RULER. In the RULER analysis we can see a curve with a perfect linear fit for the total remaining antioxidant %. This is the consequence of a direct antioxidant addition when making Refreshment samples. On the other hand, RPVOT assesses the whole oxidation condition, including antioxidants and base oil. From this, we can learn that, even though antioxidants prevent the base oil from degrading, these are not 100% effective and during the aging of the lubricant, the base oil also suffers to some extent.

Another lesson that can be learned from this analysis is the reason why lubricants form varnish before the antioxidants run short.

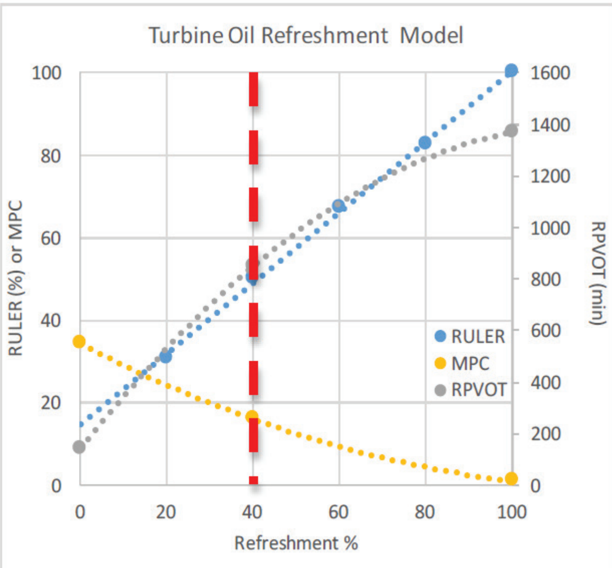


Figure 6. Refined Turbine Oil Refreshment Model.

The preliminary model is refined with experimental data for MPC and RPVOT of 40% refreshments. The RPVOT value of the refreshed sample is higher than the predicted linear model. Also, the MPC value is lower than the predicted linear model.

The MPC for a simulated 40% refreshment was reduced from ΔE = 21, as would have been expected in a linear model, to ΔE = 16. This is also a significant reduction for the varnish formation potential. It is a normal statement in the condition monitoring community that adding fresh oil to a system helps to re-dissolve varnish to some extent.

When adding fresh oil to a system the saturation of molecules with varnish potential decreases and a fraction of these dissolves in the oil. This partially explains why the MPC value drops. However, this cannot explain the observed "synergistic" effect. As explained above, the MPC procedure involves varnish re-dissolving and standardised re-precipitation.

In a refreshment sample, varnish becomes more diluted, and this results in a slower re-precipitation, which can influence the MPC reading. To test this, 40% refreshment samples were heated at 60ºC for 24h and stood to precipitate for either the standard 72h or for 168h.

Figure 8 shows that after a one week precipitation, the MPC values rises, indicating that the precipitation did not reach an endpoint after 72h.

Given that the rate of precipitation is slower when samples are diluted with fresh oil, the "synergistic effect" in the MPC value observed in the refreshment plot is probably due to this phenomenon.

To further assess on this phenomenon, refreshment plots were made for the MPC value of samples precipitated for either standard 72h or experimental 168h (Fig 8b).

Interestingly, the refreshment plots for the 168h precipitation are linear (Rsq = 0,9996), a fact that correlates with the simple dilution effect.

In conclusion, in laboratory procedures, oil refreshment does not have a synergistic effect on varnish solubilisation.

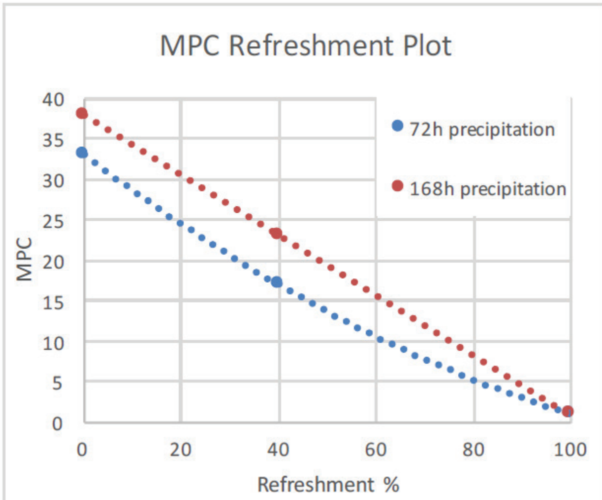


Figure 8. MPC is a standardised method in which precipitation time is critical (part II).

40% refreshment samples were heated for 24h and stood for either 72h or 168h before filtering. Refreshment plots for 72h or 168h precipitation are built together with the data from Fig. 1.

When samples are precipitated for 72h, the 40% refreshment MPC value is lower than that predicted by a linear model. Conversely, when the samples are precipitated for 168h, the refreshment plots are linear, correlating to simple dilution.

Varnish dissolves in and out of the oil as a function of temperature. When scaling the results to an actual turbine, we should bear in mind that refreshed oil will decrease the varnish saturation, and at operation temperatures, may solubilise varnish deposits in the system.

For this reason, after lubricant refreshment, it is usual to find a preliminary fall in the MPC value, which rises according to deposits that are solubilised. Even though from the lubricant condition perspective this looks as if there has been no progress, from the turbine condition perspective, the lubricant is chemically removing varnish from surfaces, which is indeed a desirable effect.

The best practice in this case is to couple the turbine to a varnish mitigation system.

REFRESHMENT PROPOSAL

After studying the full model, we are prepared to propose the intervention on the turbine by refreshing 40% of the lubricating oil. This option will result in a 50% antioxidant charge, a RPVOT of 849 minutes and an MPC of 16.

Under this condition, the turbine is equipped for lean operation in the short term. However, given that the original MPC is very high, it is reasonable to think of deposits in the turbine surfaces redissolving.

This might rise in the MPC in the short term, hence it is recommendable to install a varnish mitigation system together with the oil replenishment.

Refreshment models allow us to analyse turbine oxidation condition in depth. This results in understanding the potential of an in-service oil and the expected performance of the turbine in the short and midterm, focusing on the prevention of varnish and on reliability enhancement.

Finally, the methods allow us to propose maintenance actions: an exact and educated oil refreshment and recommendations on varnish mitigation.

REFRESHMENT STRATEGIES

Different to the commissioning of new turbines, refreshment studies are applied to operating machinery in which every case study is different. Differences arise in the condition of the turbine, in the maintenance and economical strategy of the machinery owner and in the available services in each region There are several strategies for maintaining high doses of antioxidants and oxidation condition within reliability parameters. The first line in keeping the antioxidants high is the regular lubricant top-off.

This makes up for about 5% of the lubricant per year.

In each addition, fresh antioxidants are introduced into the system. However, 5% each year does not usually satisfy the total oxidation rate in a turbine, so an additional strategy must be applied.

There are two possible paths to follow: either bleed and feed or antioxidant replenishment. Bleed and feed is the conservative option. This option is expensive from an economical perspective, because when bleeding oil from the turbine, unless the oxidation has gone too far, the base oil molecules are usually not oxidised (Livingstone, 2014)

In this way, even though only the antioxidants (1%) needed refreshment, the bled base oil (99%) is wasted. The other cons in bleed and feed are that when an oil refreshment of 30% or more is needed, the antioxidants in the new oil refresh oxidised antioxidants both in the in-service oil and those forming reversible deposits.

In this way, 1000h after refreshment, the dosed antioxidant tends to be less than expected. However, performing bleed and feed is the safest procedure for refreshing the lubricant. When performing bleed and feed, as long as the same lubricant and good lubricating practices are followed, there are no concerns about formulation-derived incompatibilities.

Even though the procedure may be expensive, it is acceptable for many industries. Also, bleed and feed is a fast operation. Depending on the turbine and on the required refreshment %, bleed and feed can be done without stopping operation or with minimal down time.

The second possible strategy is additive replenishment. In this strategy, an antioxidant concentrate is slowly fed to the turbine oil with minimal in-service oil bleed. In this way, the base oil is conserved, and antioxidants are re-dosed to a desired level.

This strategy must be carried by an experienced formulator who has an intimate knowledge of the chemistry of the base oil and the antioxidants in the system, and the chemistry of the deposits formed in the particular system.

Additive chemistry is a complex science: as we have shown, additive chemistries interact, and this interaction can be either synergistic or antagonistic. Synergy accounts for the regeneration of aminic front-line antioxidants by fresh phenolic antioxidants. On the other hand, when turbine oil forms varnish, these are heavily composed of both fresh and oxidised antioxidants.

When reformulating in-service oil, it is of utter importance that formulation-derived deposits are not formed. One major issue to take into account, is that when adding antioxidants to an in-service oil, the total antioxidant concentration, dead or alive, rises and, without keen knowledge of the system, this may easily result in antioxidant precipitation or undesired reactions between antioxidant species taking place inside the turbine to form varnish.

To achieve high reliability, the compatibility and performance of both the concentrate and the reformulated oil must be extensively tested in a laboratory. Testing must include characterisation of the resulting physical properties, functional properties such as foaming, air release, demulsibility and prognostics on the ageing and resulting oxidation condition of the reformulation.

Lastly, tests defying deposit formation must be passed. Once the chemistry of the additive replenishment is adequately tested, the in-plant execution must be carefully driven by recognised technicians. This accounts for assuring adequate mixing of the fluids, avoiding precipitation, and having a contingency plan if deposit formation should arise.

CONCLUSION

In conclusion, additive replenishment is the best option from the economical perspective. From the technical perspective, excellent results are achieved, and successful projects have multiplied the in-service period of turbine oils. However, it is a practice that implies higher risks and is usually planned and executed by third-party services.

Even though gas and steam turbines are spread throughout the world, it is not possible to find adequate laboratory services for testing and technical services for in-plant executing these projects in all regions. In these cases, even though economically more expensive, bleed and feed procedures continue to be carried out.

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