

## Water + Grease = fatal attraction?



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## ABSTRACT

*In the real world, it is often difficult, if not impossible, to avoid the ingress of water into bearings and other types of machine elements. The ability of a lubricating grease to withstand, reject or absorb water can therefore be vital to optimal performance in many areas. Using generally available laboratory standards, lubricating greases with different thickener systems have been tested to compare their ability to perform even when contaminated with water. The results are then matched with experiences from real life applications and conclusions drawn on how to select greases for use under wet conditions.*

## INTRODUCTION

When we were presented with the theme for the 25<sup>th</sup> ELGI AGM “*Water, problem solved?*” we started looking at what we could present. The first, and most obvious, thing that came to mind was that we know how well our products perform in real applications, but how does this match the laboratory test results for the same products? We therefore decided to perform this study where we analyse the effect of water ingress on five commercial products and compare this with data from real applications.

With this study we don’t aim at resolving the issue of how bad, or good for that matter, water contamination is in general. What we hope to achieve is to give a balanced picture of how five different greases with a track record from real applications, perform in laboratory tests when contaminated with water. By combining field test data with laboratory data we then hope to be able to give some general advice concerning which greases that are preferred when there is risk of water ingress. A secondary topic that we also will get into is how water is taken up by greases and which components facilitate the incorporation of water into the grease matrix.

Searching for information and literature related to the performance of lubricating greases that have been contaminated by water does not give many references and the information available is not very conclusive. In some cases it is stated that “*as little as 1% water in grease can have significant impact on bearing life*” [1, 2]. Other sources are a little more specific in stating that corrosion protection, consistency, texture and adhesiveness might be affected by water ingress and that the contaminated grease “*probably is an inferior lubricant*” [3]. A more balanced description is given by P. Lugt who writes “*some greases perform well with large quantities of water absorbed, others do not*” [4]. When it comes to studies looking at real applications, it is even harder to find any published results. In steel rolling mills the loss of consistency when water is emulsified into the structure seems to be an issue for most types of greases [5]. On the other hand, in an aviation jackscrew application no increased wear was seen when contaminating both lithium complex grease and a clay thickened grease with water, de-icing fluid or salt-water [6]. For an overview of laboratory methods for testing water stability and technologies used in water resistant greases there is a White Paper from Axel Christiernsson from 2008 [7].

In real applications, we encounter water in many different forms: From rain, snow, sea water to process liquids containing various chemicals. For time reasons we had to limit ourselves to looking at contamination by pure water in the experimental part of this investigation. What one should keep in mind is that industrial process liquids can affect greases quite differently compared to what we observed in this study where we used distilled water.

## MATERIALS and METHODS

### Grease selection

The five different greases selected for this study are presented in *table 1*. All the greases have a similar NLGI grade and are all commercial products. The first grease, identified as *PP* hereafter, is a synthetic grease thickened with polypropylene. In contrast to the other four greases this product has not been developed with water resistance in mind. The second grease (*LiX*) is lithium complex soap thickened and has a mineral base oil. The next is an anhydrous calcium thickened grease in a mineral oil (*Ca-Min*). The fourth is a calcium sulphonate complex grease (*CaSX*) and the last is another anhydrous calcium thickened grease, but this time with a biodegradable ester as base oil (*Ca-Bio*).

| <b>Identifier</b> | <b>Thickener</b>           | <b>Base oil</b>     | <b>BOV at 40°C</b>    | <b>Tackifier</b>                                                                                 | <b>NLGI</b> |
|-------------------|----------------------------|---------------------|-----------------------|--------------------------------------------------------------------------------------------------|-------------|
| <b>PP</b>         | Polypropylene              | Polyalphaolefin     | 200 mm/s <sup>2</sup> | Hydrogenated styrene-diene (STD)                                                                 | 1.5         |
| <b>LiX</b>        | Lithium complex            | Mineral Oil         | 750                   | Olefin copolymer (OCP)                                                                           | 1.5         |
| <b>Ca-Min</b>     | Anhydrous Calcium          | Mineral Oil         | 1300                  | Polyisobutylene (PIB)                                                                            | 1.5         |
| <b>CaSX</b>       | Calcium sulphonate complex | Mineral Oil         | 220                   | PIB + STD                                                                                        | 2           |
| <b>Ca-Bio</b>     | Anhydrous Calcium          | Biodegradable ester | 540                   | Styrene-Ethylene/Butylene-Styrene block copolymer (SEBS) and partially polymerised vegetable oil | 1.5         |

**Table 1:** The five selected greases for this study.

### Mixing grease and water

Distilled water was mixed homogeneously into the grease using a DAC600 SpeedMixer. The mixing cycle was 1800 rpm for 5 minutes and this was repeated until the sample became homogeneous. Before any of the samples were analysed, entrapped air bubbles were removed by mixing at 800 rpm for 3 minutes for the two products that were most affected by the water (PP and LiX) and 1000 rpm for 3 minutes for the remaining greases.

### Standard grease tests.

In this study we evaluated the greases using a number of tests that are common to the grease industry. In *table 2* these tests and the corresponding standards used are listed.

| <b>Test</b>                  | <b>Condition</b>      | <b>Standard</b>                   |
|------------------------------|-----------------------|-----------------------------------|
| Penetration after 60 strokes |                       | ISO 2137                          |
| Shell roll stability         | 80°C for 50h          | ASTM D1831 modified <sup>1</sup>  |
| Water washout                | 79°C                  | ISO 11009                         |
| Water resistance             |                       | DIN 51807:1                       |
| Water spray off              | 38°C                  | ASTM D4049                        |
| Flow pressure                | -20°C                 | DIN 51805                         |
| Emcor                        | 3% synthetic sea salt | ISO 11007                         |
| Copper corrosion             | 100°C for 24h         | ASTM D4048 modified <sup>2</sup>  |
| 4-ball weld load             |                       | DIN 51350:4                       |
| 4-ball wear scar             | 400N for 1h           | DIN 51350:5 modified <sup>3</sup> |
| Dropping point               |                       | IP 396                            |
| Oil separation               | 40°C/168h             | IP 121                            |

**Table 2:** The common grease tests and the corresponding standards used in the analysis of the samples. <sup>1</sup>Test run at 80°C for 50 h which are non-standard conditions. <sup>2</sup>Copper corrosion performed in a petri dish. <sup>3</sup>400N is a non-standard load.

### SKF R2F-A

The lubricity of the greases, with and without water, was tested using the SKF R2F-A test. In this study, due to the lack of time, the test was run in a non-standard way. Normally both test bearings (spherical roller bearings) are lubricated with the same grease and the test is then performed at ambient temperature for 20 days (8340 N radial load at a speed of 2500 rpm). During the test, the temperature profile is recorded and, after the test, roller and cage wear is measured. In this case we lubricated one bearing with water-free grease and the other with the same grease contaminated with 10% water. The advantage of this is that we save time. The disadvantage is that when one of the bearings encounters problems in maintaining a lubricating film, the increase in friction and resulting vibrations will be transferred to the other bearing through the axis. Therefore the measurement from the second bearing will be influenced by the result from the first bearing experiencing lubrication failure.

### SRV wear test

The wear test was performed on an SRV4 according to ASTM D5707-05 at 50°C. As most of the greases tested do not pass the test at this temperature, mainly due to limited oil bleed, the result from this test is judged by how large the difference is between the samples. The differences are either lower coefficient of friction or longer running time before seizure. For those samples that passed the entire length of the test the wear scars were analysed using a Bruker Contour GT-K0 optical profiler.

### Rheological measurements

*Apparent Viscosity:* After the test temperature had been reached, the sample was kept at rest for 5 minutes in order to relax the sample and give the sample enough time to adapt to the test temperature homogeneously. The shear rate  $\dot{\gamma}$  was increased logarithmically from 0.1 to 100 s<sup>-1</sup>. The apparent viscosity, which is a measure of the degree of structure of the grease, was determined at a shear rate of 1 s<sup>-1</sup>.

*Strain Sweep:* After the test temperature had been reached, the sample was kept at rest for 5 minutes in order to relax the sample and give the sample enough time to adapt to the test temperature homogeneously. The strain  $\gamma$  was increased logarithmically from 0.01 to 1000% with an angular frequency  $\omega$  of 10 rad/s. From the measurements the flow point ( $G'=G''$ ) was determined. This is the point at which the internal structure of the material is disrupted to such an extent that causes the material to flow.

### Pulsed field gradient NMR

Diffusion experiments were run on a 14.1 T (600 MHz) Bruker spectrometer equipped with a Diff30 probe at 25 °C. <sup>1</sup>H diffusion measurements were carried out in the z-direction by using a standard stimulated echo sequence. The gradient duration  $\delta$  was set to 3 ms and the time between the leading edges of the two gradient pulses  $\Delta$  was varied from 60 ms to 1 s in 5 steps. The gradient strength  $g$  was varied between 0.2 and 12 T m<sup>-1</sup> in 16 steps depending on the choice of  $\Delta$ . For each sample, 16 transients were collected. The processing (phasing and baseline correction) and integration of the water peak (4.8 ppm) was done with Matlab (MathWorks Inc., USA). The normalized peak integral  $I$  versus the diffusion-weighting factor  $b = (\gamma g \delta)^2 (\Delta - \delta/3)$  (where  $\gamma$  is the gyromagnetic ratio of <sup>1</sup>H) was used to estimate the fast and slow diffusion components,  $D_f$  and  $D_s$  by:  $I = I_0 \exp(-D_f b) + (1 - I_0) \exp(-D_s b)$ , where  $I_0$  is the fraction of the fast diffusing component.

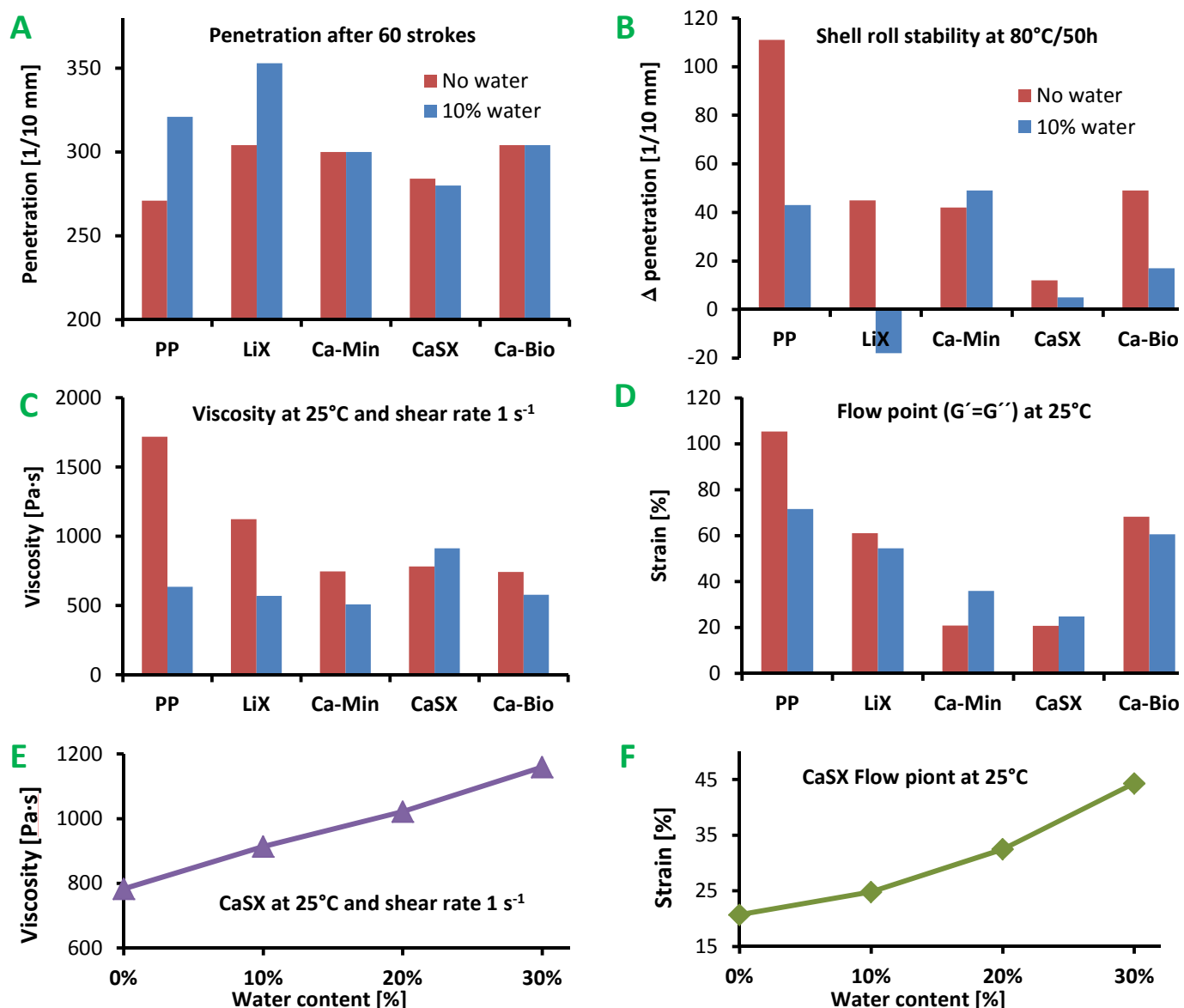
## RESULTS AND DISCUSSION

### Consistency

Two of the studied greases, the polypropylene thickened (PP) and the lithium complex (LiX) grease, became much softer in the cone penetration test when water was mixed in, whereas the remaining three greases were more or less unchanged (see *fig 1 panel A*). When measuring the apparent viscosity at 25°C and a shear rate 1s<sup>-1</sup> we got a similar picture (see *fig 1 panel C*). The viscosity is significantly reduced for samples PP and LiX, whereas we saw a smaller reduction for the two anhydrous calcium soap thickened greases (Ca-Min and Ca-Bio). In contrast, for the overbased calcium sulphonate complex grease (CaSX), we noticed a slightly increased viscosity when adding water.

If we turn to the mechanical stability of the greases there was a large improvement in roll stability for PP and LiX (see *fig 1 panel B*), but this is simply due to the fact that they lose a lot of structure when water is mixed in, the structural stability of the thickener itself is unchanged (*i.e.* the penetration value after the roll test was more or less the same with and without water). The mechanical stability of samples Ca-Min and CaSX were also unchanged by the incorporation of 10% water. Quite surprisingly we saw an improved mechanical stability for sample Ca-Bio. This stabilisation could be caused by a water accelerated polymerisation of the base oil and/or the biodegradable tackifier used.

The change in flow resistance when incorporating water revealed that the flow resistance for the PP sample was reduced to a lower strain, whereas the remaining samples were affected much less (see *fig 1 panel D*). Interesting to notice is that both samples Ca-Min and CaSX indicate a somewhat increased flow resistance.



**Figure 1:** In panels A-D red colour symbolises the samples without water contamination and the blue show data for the samples with 10% water incorporated. Panel A shows the consistency measured by cone penetration after 60 strokes. Panel B depicts the penetration difference in the roll stability tests. Panel C shows the result of the apparent viscosity test. Panel D illustrates the flow point (crossover point where  $G' = G''$ ). Finally panels E and F show the apparent viscosity and the flow point for sample CaSX at concentrations of up to 30% water contamination.

Since the increase in viscosity and flow point for the CaSX grease at 10% water ingress were small and probably within the margins of error for the tests we decided to extend the tests to samples with more water. In *panels E* and *F* are the viscosity and flow point results presented for samples with 20% and 30% water contamination as well. The trend is clear: Both the viscosity and the flow point increase with the amount of water for the calcium sulphonate complex grease.

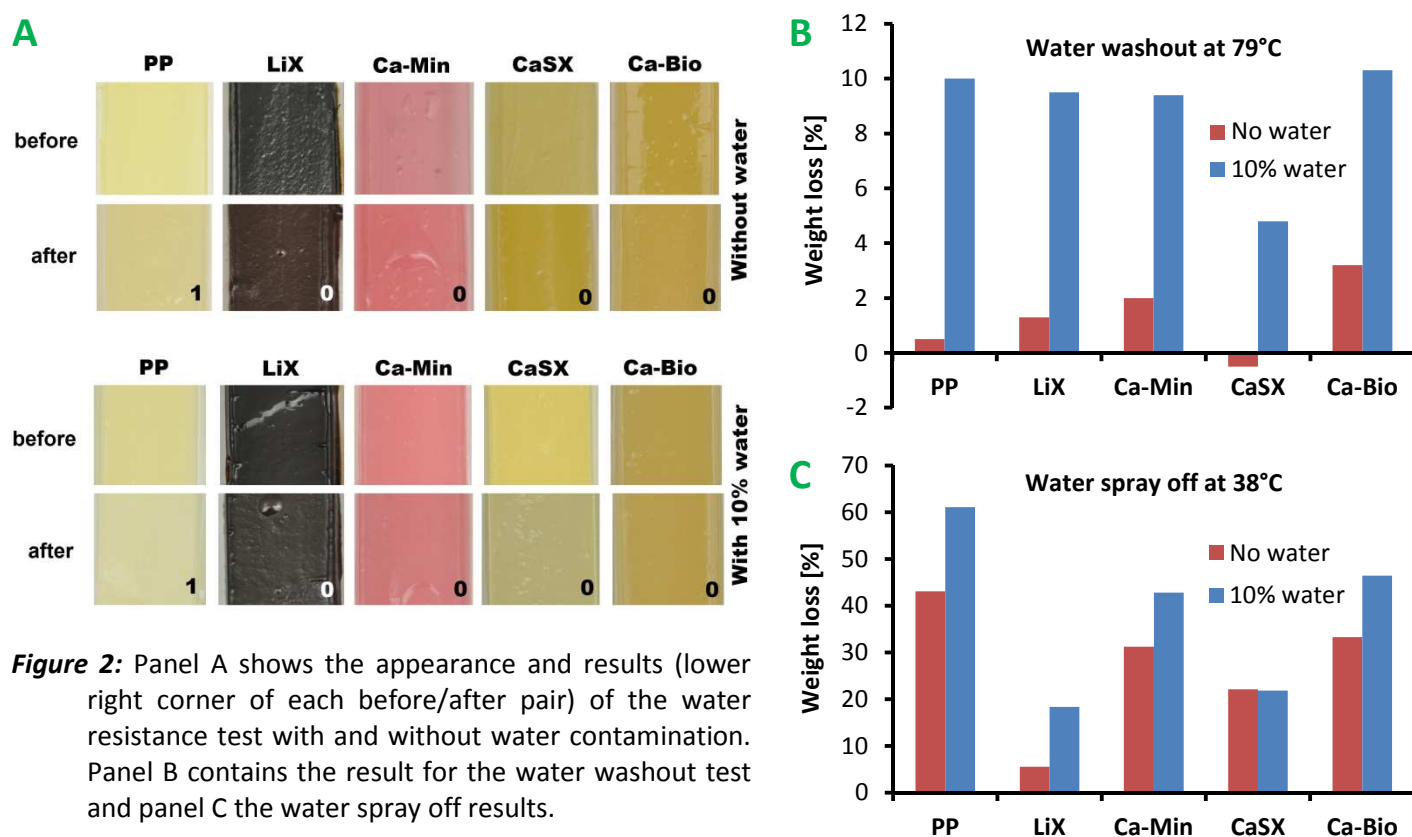
## Water tests

Three different tests that evaluate the direct response to water were run: *Water resistance* a static test that evaluates the ability of a grease to resist degradation by the action of water. *Water washout* which is a dynamic test that evaluates the resistance of being washed out from a bearing by water. *Water spray off*, a second dynamic test, that evaluates the ability of a grease to remain on a metal surface when subjected to water spray.

*Water resistance*: In the water resistance test there was no difference between the water free and the water contaminated samples (see *fig 2 panel A*). All results were unchanged.

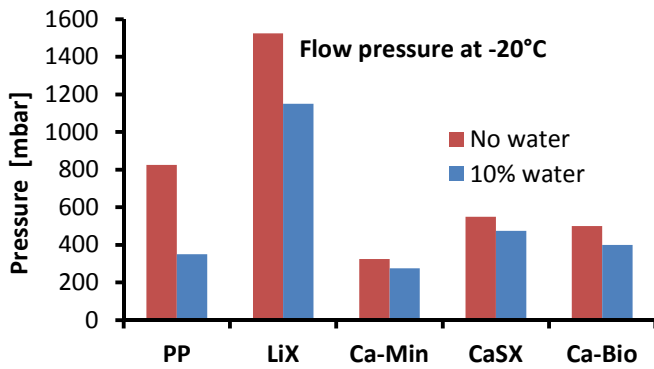
*Water washout*: All greases performed worse in the water resistance test when contaminated with water (*fig 2 panel B*). Even the CaSX sample that became thicker and more flow resistant when contaminated with water lost more grease in the water washout test when contaminated with 10% water. The negative weight loss seen for the water free CaSX sample indicates that more water was absorbed by the grease than the amount of grease that was lost during the test.

*Water spray off*: In the water spray off test there is one grease that sticks out and that is the CaSX sample that was unaffected by 10% water incorporation (see *fig 2 panel C*). The other four greases all exhibited significantly more spray off when contaminated by water.



## Low temperature

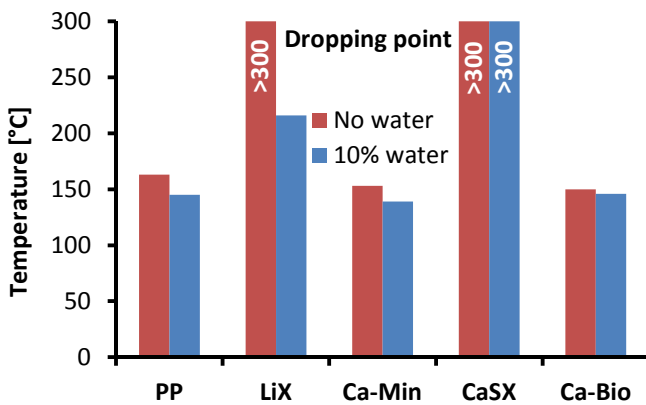
Instinctively one might think that at sub-zero temperatures a grease contaminated with water should suffer in the flow pressure test, but this was not the case. Actually, all five greases performed better in the flow pressure test when contaminated with water (see *fig 3*). This result might not be too surprising for samples PP and LiX since they lost a lot of consistency when contaminated with water, but the same result was also seen for Ca-Min and Ca-Bio and even for CaSX which displayed an increased consistency at 25°C when contaminated with water. A possible explanation for the improved flow pressure results is that the entrapped water is disturbing the crystallisation of the base oil, thereby reducing the consistency increase of the grease at low temperatures



**Figure 3:** The results from the flow pressure test at -20°C.

### Dropping point

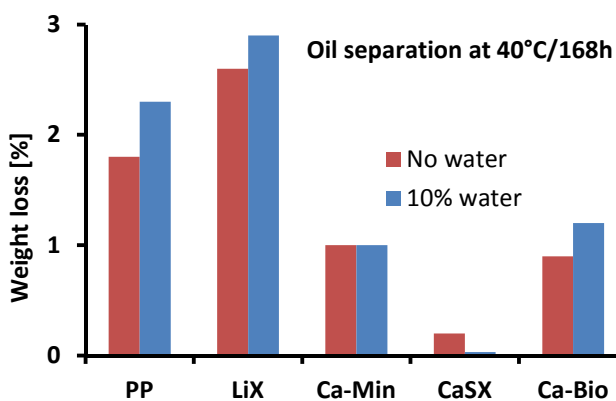
In the dropping point test we saw a decrease in dropping point by more than 65 C° for the LiX sample (*see fig. 4*). For the PP and the Ca-Min samples we saw smaller changes in dropping point (15-20 C°) and for the CaSX sample we see no difference with the test method that we ran. Finally, the Ca-Bio sample displayed an almost unchanged dropping point.



**Figure 4:** The results from the dropping point test at -20°C. Three of the samples had a dropping point over 300°C which is indicated in the figure by the text ">300".

### Oil Separation

In the IP121 oil separation we only noticed subtle differences between the samples (less than 0.5% difference for all samples).



**Figure 5:** The results from the one week oil bleed test at 40°C.

## Ferrous corrosion

For corrosion testing we ran the SKF Emcor test with synthetic sea water (see Fig. 6). The result from this test was that the contamination of water did not have any effect on the corrosion protection of the greases tested.

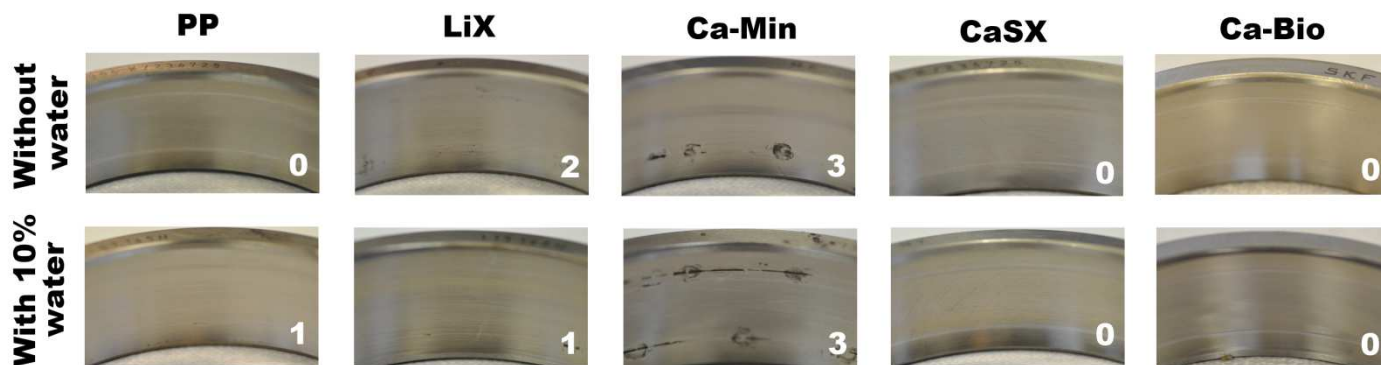


Figure 6: The bearing raceway after the SKF Emcor test with 3% synthetic sea water.

## Copper corrosion

In the copper corrosion test the PP and LiX samples gave unchanged results with and without water. For the greases which contain calcium soap the story is quite different. For all three samples we saw a large drop in performance. Ca-Min and CaSX changed from stage 1 to stage 3 and Ca-Bio, which had poor copper corrosion performance to start with, changed from 3a to 3b.

What is causing the staining in the calcium containing products with water is not completely understood. Tests done with a calcium sulphonate grease (not a calcium sulphonate *complex* grease), a synthetic distearate in oil and a pure anhydrous calcium grease without any additives at all (samples outside this study; data not shown) point in the direction that the additives are the cause of the staining. Further investigations are needed to fully understand what the cause is.

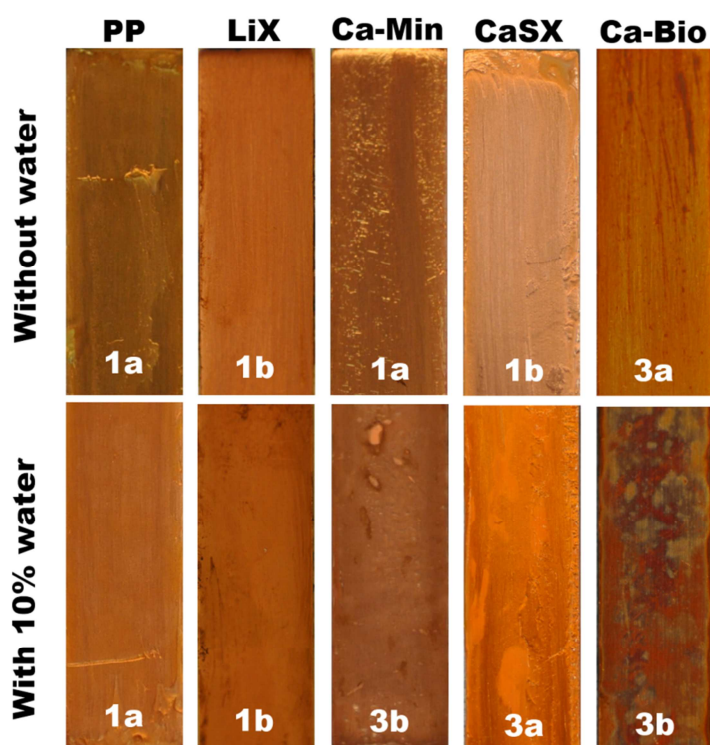
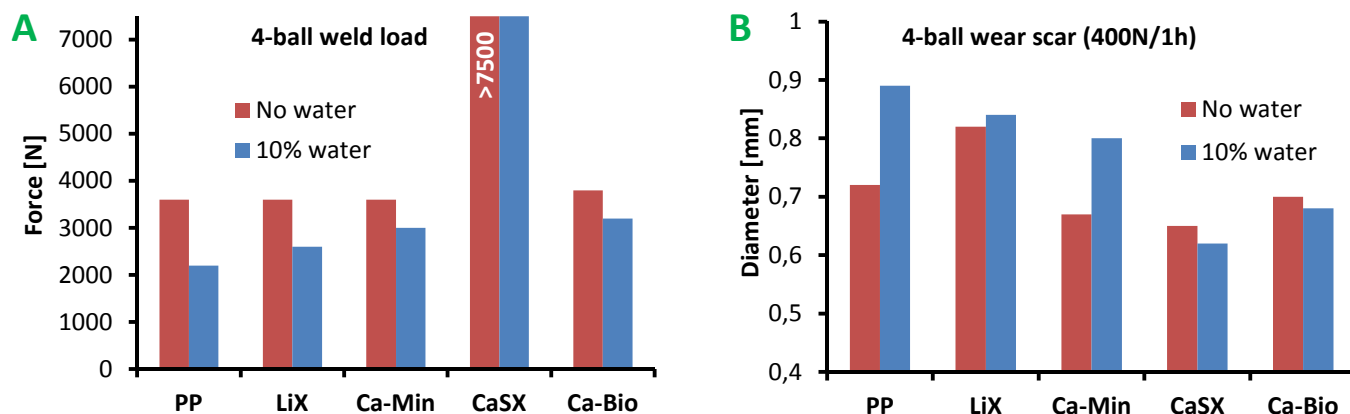


Figure 7: The results from the copper corrosion test at 100°C for 24h.

## Extreme pressure and Anti-wear

**4-ball weld load:** In this test all greases had a lower weld load when contaminated with water (see *fig. 8 panel A*). Samples PP and LiX showed the largest drop in weld load (1400 and 1000N, respectively). The two anhydrous calcium greases (Ca-Min and Ca-Bio) lost 600N in weld load. For sample CaSX we could not determine the exact decline in weld load as the water free product passed at higher loads than our 4-ball machine can apply. Contaminated with water, the CaSX sample welded at 7500N.

**4-ball wear scar:** The result from the wear scar test run at 400N for one hour was that the wear scars for three of the products remained unchanged (see *fig. 8 panel B*). For the PP and Ca-Min greases we saw increased wear scars.

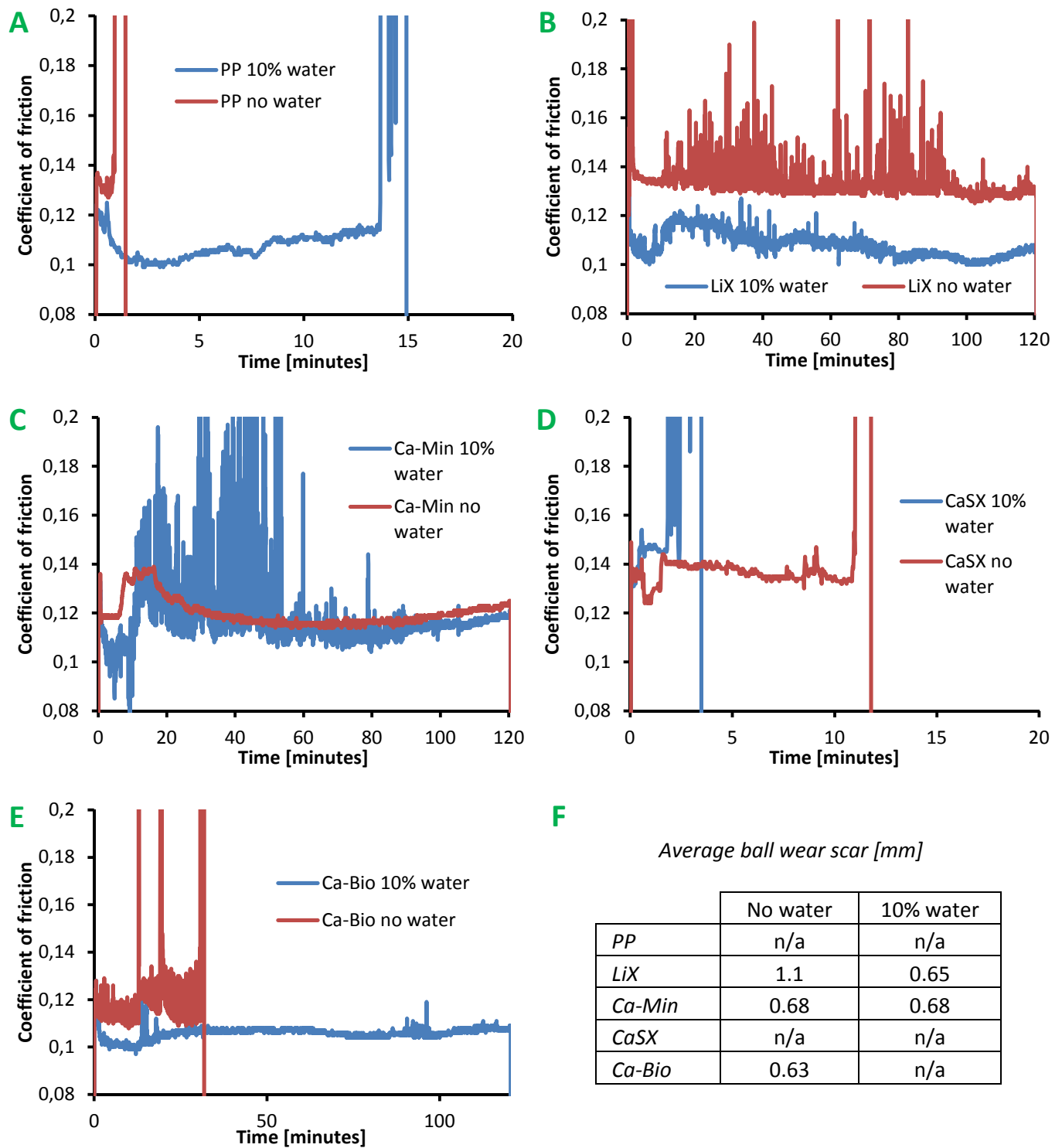


**Figure 8:** Panel A illustrates the result from the 4-ball weld load test where all greases show a lower weld load when contaminated with water. The label “>7500” indicates a weld load higher than the range of the 4-ball machine. Panel B shows the wear scar diameter from the 4-ball wear test.

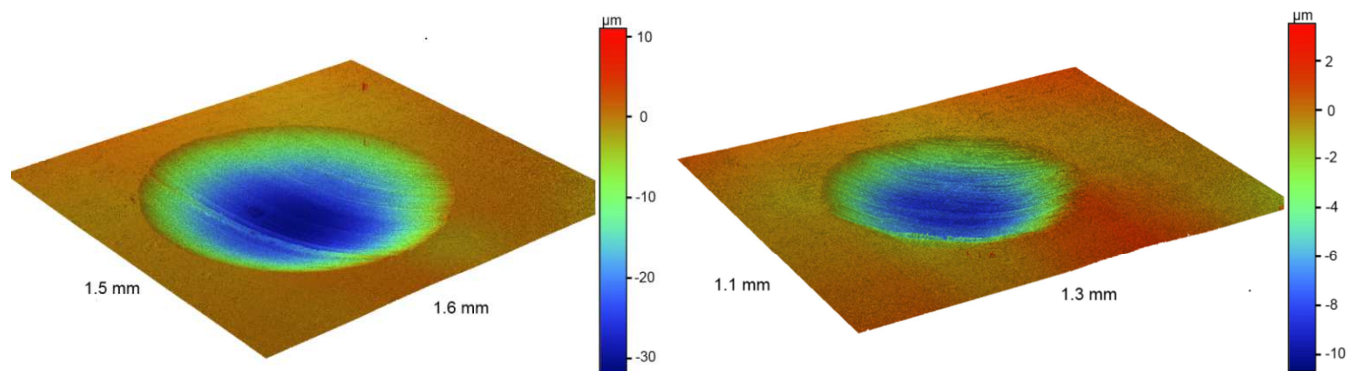
**SRV wear measurements:** Most of the greases in this study are not very good in the SRV wear test to start with, especially not at 50°C as the oil bleed from these greases is very low. Nevertheless, we decided to run the SRV wear test for all the greases to see if there would be any differences between the water contaminated and water free greases. As only half of the products pass the wear test, the results from these tests will have to be judged quite subjectively – is there an improvement or not. To our surprise all but two greases had improved performance in the SRV wear test.

With the combination of a nonpolar thickener and a nonpolar baseoil the PP grease (*fig. 9 panel A*) has poor performance in this test. The addition of water improved this significantly, prolonging the time until failure. For the lithium complex grease (see *fig. 9 panel B*) we noticed larger improvements when adding water – a reduced coefficient of friction and a smaller wear scar (see *fig. 10* and *fig. 9 panel F*). Sample Ca-Min displayed a much rougher coefficient of friction profile with water, but the ball wear scar remained unchanged (see *fig 9 panels C* and *F*, respectively). The calcium sulphonate complex grease was the only sample that performed worse with water in the grease (*panel D*). The greatest improvement was seen for the Ca-Bio sample where a failed test with the uncontaminated grease turned into a passed test with good wear characteristics (see *panels E and F*).

In this study, the SRV wear test was performed at 50°C to avoid evaporating the water. In general, all greases would perform better in the test at higher temperatures, due to increased oil bleed leading to more oil in the contact zone. Therefore, it might feel a little counter intuitive to speculate in, whether or not, the improved results, for at least some of the greases, might be due to a cooling effect. Here one should probably differentiate between the temperature of the grease and the temperature directly in the contact zone. A lower temperature of the grease itself is not advantageous, but a lower temperature in the contact zone, due to the evaporation of water, might very well improve the results. Looking at the curves with improved results there is a segment, during the first 10 minutes or so, where the friction is significantly lower (this is particularly visible in *panels B* and *C*). This reduced friction could very well be a reduction caused by the presence of water in the contact zone, which after 10 minutes has evaporated.



**Figure 9:** Panels A to E show the coefficient of friction plotted against time for the five samples. Not to clutter up the figures too much we only show one profile per sample, but we have run at least two runs per sample to verify the results depicted. The ball scar diameters are given in panel F for the samples that made it through the entire 120 minutes of the test without seizure.



**Figure 10:** Example of a 3D surface representation illustrating the ball wear scar difference between a water free and water contaminated LiX sample. The average ball wear scar diameter for the sample without water is 1.1 mm (left figure) and average wear scar diameter with 10% water is 0.65 mm (right image).

## Lubricity

The lubricating ability of the grease is naturally one of the most important features and we evaluated this using the SKF R2F-A test rig. In this study the test was not run according to standard procedure due to the lack of time. Normally both of test bearings are lubricated with the same grease, but here we ran the water free grease on one side and the water contaminated grease on the other side. This deviation from procedure has some disadvantages. When the first bearing in the test rig runs into lubrication issues - loss of lubricating film, resulting in friction, heat and vibrations – this disturbance will be transferred to the other bearing via the shaft. This can for example be seen quite clearly in the last five days of the test for sample PP (*fig. 11, panel A*). Due to this transfer between bearings we will have to focus on the differences between the water contaminated and the water free bearing without putting too much focus on the exact numbers.

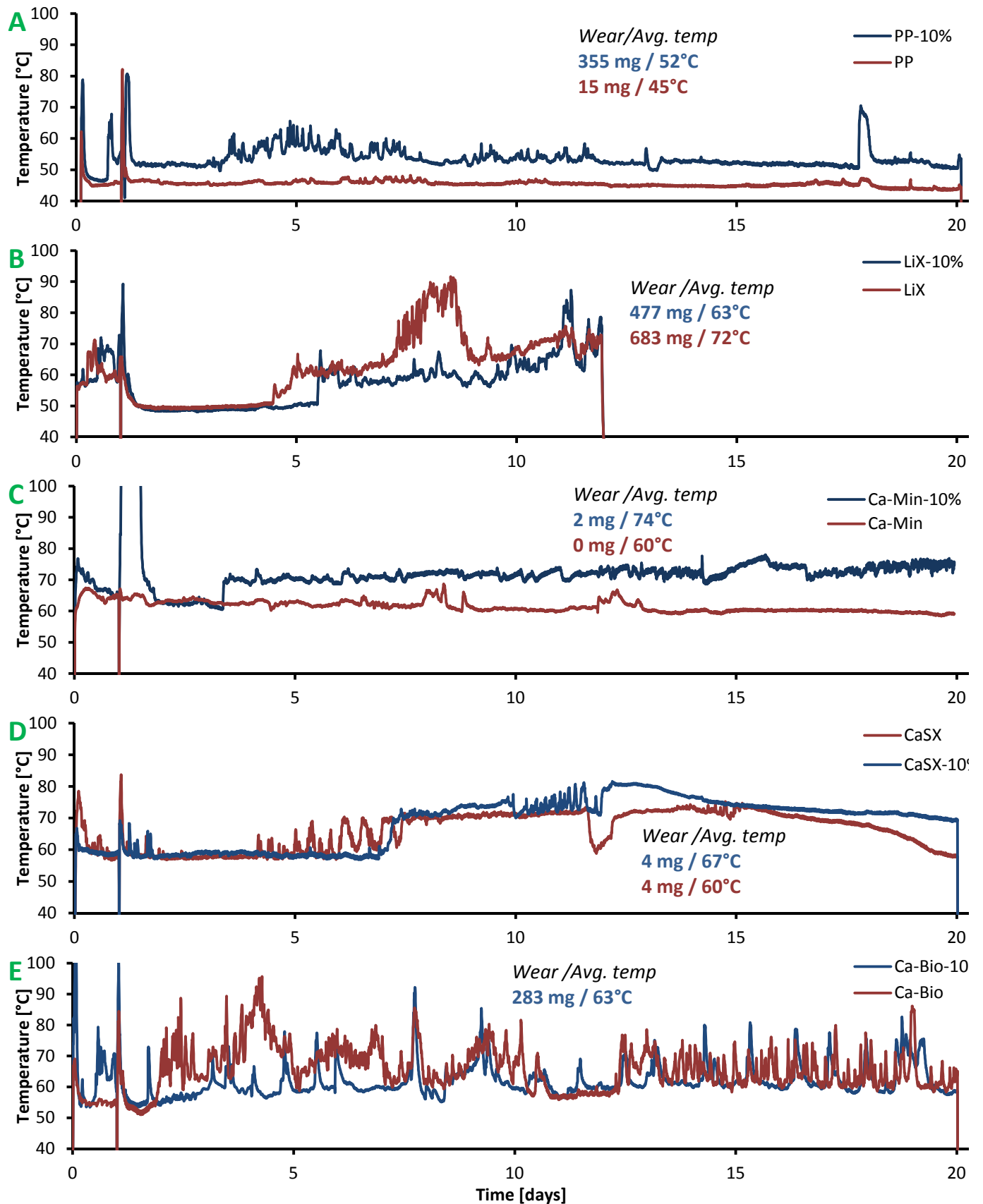
For the PP sample (*panel A* below) water did not help lubrication in the R2F-A test. The average running temperature during the last five days increased and so does the wear. For the lithium complex grease (*fig. 11 panel B*) the result was the opposite. In the sample with water both wear and running temperature were reduced. However, as can be seen in the figure this test stopped after 12 days as the grease sample without water had become so tacky and thick that the test rig stopped. For the Ca-Min sample (*panel C*) we saw only an increased running temperature for the water contaminated sample, wear was unaffected. The wear was also unaffected for the calcium sulphonate complex, which ran at a slightly elevated temperature when contaminated with water (*panel D*). The last sample, Ca-Bio, had an unchanged running temperature, but the wear was reduced significantly.

## Summary of the laboratory tests

If we summarize the results from the tests it is quite clear that, of the five greases studied, the three greases containing calcium soaps deal better with water than the PP and the LiX samples. There is only one test where the results for Ca-Min, CaSX and Ca-Bio became a lot worse and that is the copper corrosion test. If a best-in-test grease would have to be selected at this point it would be the last sample, Ca-Bio, which actually performed better when contaminated by water.

|                   | <i>PP</i> | <i>LiX</i> | <i>Ca-Min</i> | <i>CaSX</i> | <i>Ca-Bio</i> |
|-------------------|-----------|------------|---------------|-------------|---------------|
| Consistency       | -2        | -2         | 0             | 0           | 0             |
| Water tests       | -2        | -2         | -             | 0           | -             |
| Low temperature   | +         | +          | +             | +           | +             |
| Dropping point    | -         | -2         | -             | 0           | 0             |
| Oil separation    | 0         | 0          | 0             | 0           | 0             |
| Ferrous corrosion | 0         | 0          | 0             | 0           | 0             |
| Copper corrosion  | 0         | 0          | -2            | -2          | -2            |
| EP/AW             | -         | +          | -             | -           | +             |
| Lubricity         | -         | +          | -             | 0           | +2            |

**Table 3:** A summary of the changes noticed between the samples with and without water.



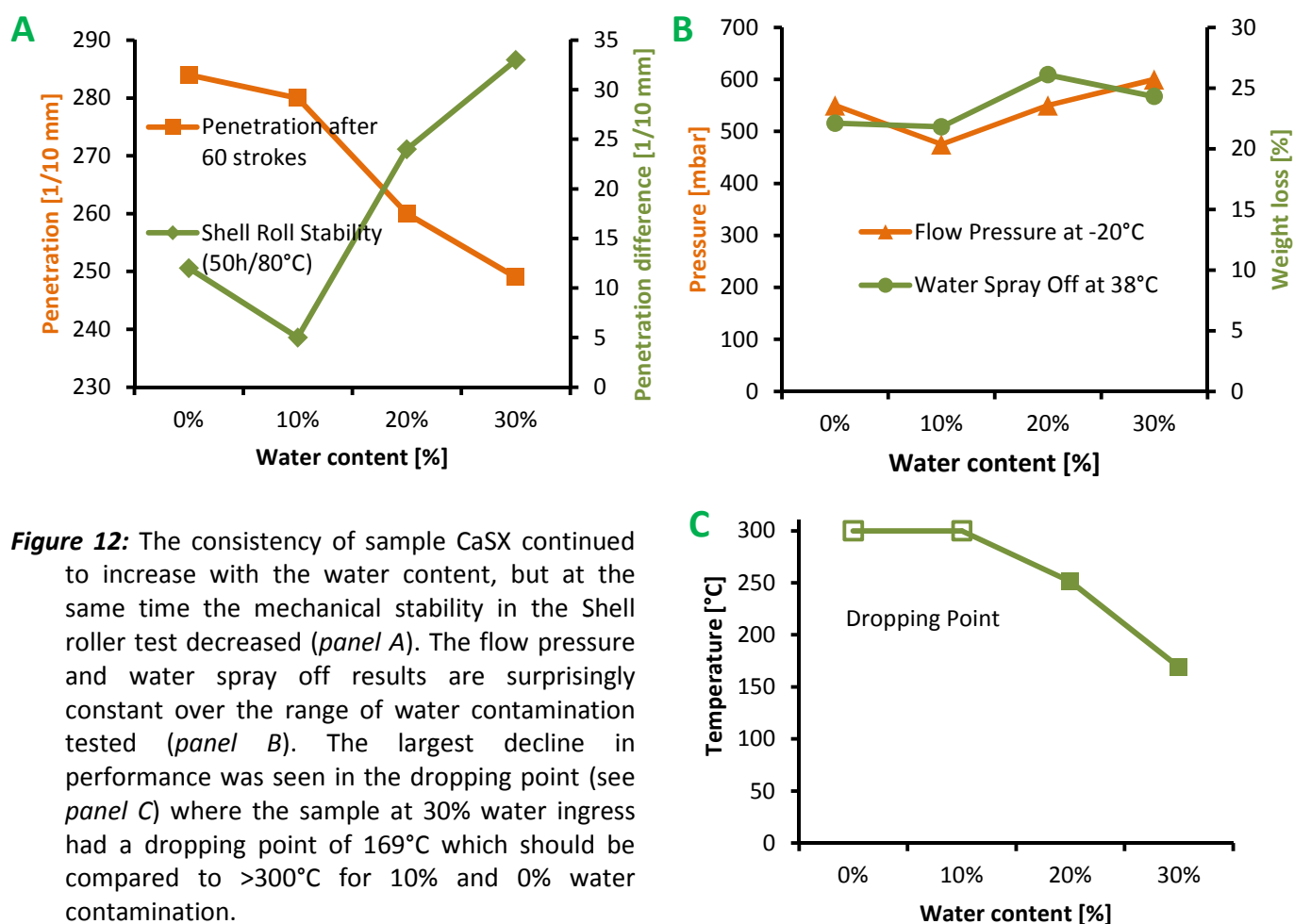
**Figure 11:** Panels A to E contain the temperature profiles from the SKF R2F-A test for all five samples. The inset in each panel gives the total wear during the entire test and the average running temperature during the last five days of each test. Blue curves and text show data for water contaminated samples and red curves and text for the water free samples.

## CaSX with more water

One thing that also has been pointed out by others [4, 5], is that calcium sulphonate greases have the potential to emulsify very large quantities of water. As a small sidetrack we therefore decided to investigate how our calcium sulphonate complex sample would behave in some of the tests if we increased the amount of water up to 30%.

The increase in consistency which was noticed in the penetration after 60 strokes for the sample with 10% water ingress continued when the water content increased (see *figure 12 panel A*). This is also in line with the viscosity and flow point data presented earlier in *figure 1 panels E and F*. That mechanical stability decreases with increased water content (*figure 12, panel A*) is maybe not too surprising. What can be noted is that the consistency after the shell roll test was, more or less, the same for all samples with water contamination. This tells us that either the mechanical stability of the grease is affected by the presence of water or that water does not stabilise the grease that has been worked in the shell roller to the same extent. Which of these two mechanisms is dominant is not possible to tell from these results.

The results from flow pressure at -20°C and water spray off highlight how differently this type of grease copes with water. The results from both tests were, more or less, unchanged between 0 and 30% water contamination. The only result where we saw a clear deterioration was in the dropping point test (*figure 12, panel C*) where the dropping point has gone down to 169°C at 30% water ingress. From the samples tested here it seems like the CaSX grease can emulsify significantly more water, probably up to 60-70%, without structurally collapsing.



**Figure 12:** The consistency of sample CaSX continued to increase with the water content, but at the same time the mechanical stability in the Shell roller test decreased (*panel A*). The flow pressure and water spray off results are surprisingly constant over the range of water contamination tested (*panel B*). The largest decline in performance was seen in the dropping point (see *panel C*) where the sample at 30% water ingress had a dropping point of 169°C which should be compared to >300°C for 10% and 0% water contamination.

### Field trials - How about reality?

All five greases tested in this study are fully formulated products that are used routinely in various industrial applications – many of them wet. So, how does the data collected from field use compare to what we see in the lab tests? Let's start with our "best in test" grease the anhydrous calcium grease with a biodegradable ester as base oil (Ca-Bio). Since this is a grease with a very good biodegradability its main use is in loss lubrication where there is risk for contamination of soil and watercourses when a normal grease is used. Therefore Ca-Bio is, for example, used very successfully in forestry applications where it is often very wet, both in the form of rain and snow. Here it is used as a general lubricant for forestry machinery and especially as a saw chain grease for harvesters. Another area of use is off highway machinery, another often wet environment.



**Figure 13:** Left: The saw chain in a harvester lubricated with Ca-Bio. Right: Forestry machine where Ca-Bio is used as a general lubricant.

For the calcium sulphonate complex grease (CaSX) tested we don't have any specific field data, but since it is used all around the world as a marine multipurpose product this is probably enough merit on its own.

The polymer grease did not do too well in this study - loss of mechanical stability and lubricity when contaminated with water. Field data on the other hand does not support this result. We have seen extremely good results in cold rolling steel mills and aluminium rolling mills (see *fig 14, top*). One reason for this difference could be the nature of the process water used in these applications. In this study we are contaminating the greases with 10% distilled water, but in both steel and aluminium rolling oil-in-water emulsions are used. The surface active components that stabilise the emulsions can be aggressive to the soap thickener leading to a collapse of the thickener structure. In the case of using a nonpolar thickener like polypropylene the effect of these surface active components is less severe. In addition to working well in applications with emulsions the PP grease also works well in wet industrial environments with other types of process water like in the wire section of a paper machine (see *fig.14, bottom*).

The anhydrous calcium thickened grease with mineral oil has a performance which is very similar to the other anhydrous calcium grease in this study (Ca-Bio). It is also used in the same way and has a very similar track record in applications. The largest difference here is that the Ca-Bio version has an environmental advantage in applications where the grease is lost into the environment.

The LiX product is also used in many wet applications like off-highway equipment and mining applications, but is also used in hot and wet applications for example in steel mill bearings and drills. We only have limited information from real applications for this product, but as far as we can tell it is performing as expected.



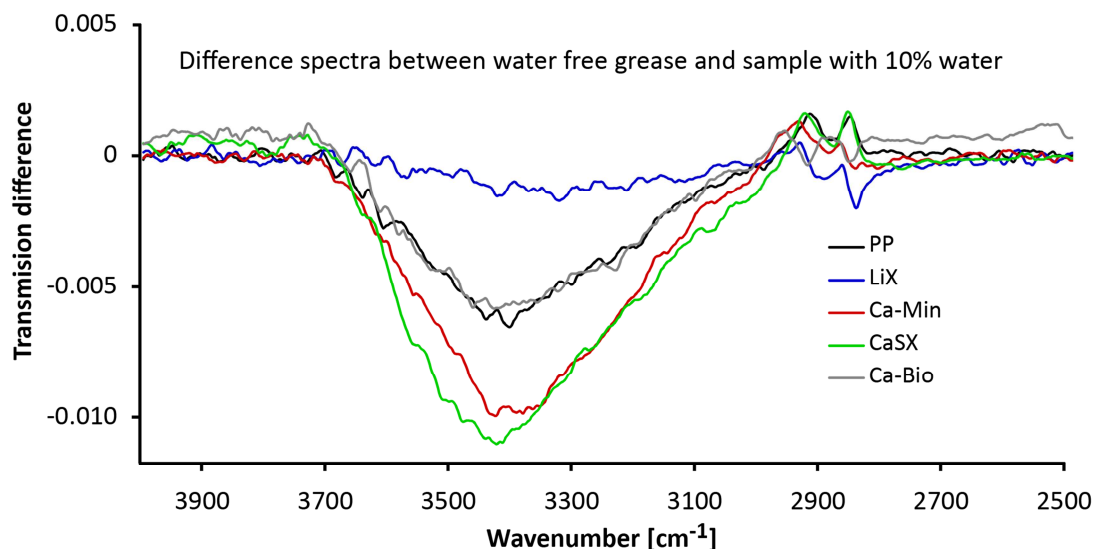
**Figure 14:** *Top left:* The bearing from a steel rolling mill disassembled after four shifts without relubrication. Normally lubrication is required several times per shift. *Top right:* In an aluminium rolling mill the PP grease softened less than the reference calcium sulphonate grease used. In addition, the problem with calcium ions staining the aluminium profiles was solved. *Bottom left:* The polymer grease used in the wire section of a paper machine where the reference lithium complex grease (*bottom right*) struggled with dry running.

### Water – how is it taken up?

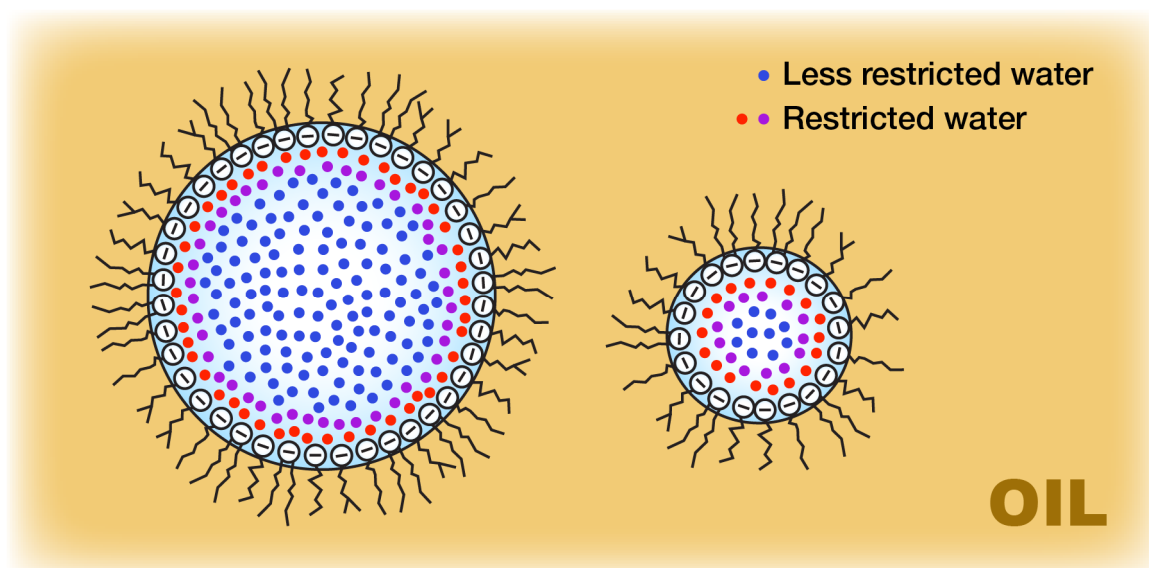
The most likely explanation is that we are creating some type of water-in-oil emulsion when we mix water into the greases. To create a stable water-in-oil emulsion there normally needs to be some kind of surface active component present. In the case of greases there are a number of polar components that could work as surface active agents and thereby facilitate the creation of an emulsion.

The first component that comes to mind is probably the thickener systems. Here the soaps in both the lithium complex and the anhydrous calcium greases could stabilise the emulsion. The calcium sulphonate complex grease also contains calcium soap, but a more probable surface active component is the sulphonate part of the thickener which is actually made from a detergent. The additives are commonly polar compounds and these might have surface active properties. Some of the tackifiers (*e.g.* STD and SEBS) might also have the ability to stabilise emulsions. The base oils are less likely to be involved in stabilising the emulsions but the more polar oils, like the biodegradable esters, cannot be ruled out. Since the tested greases all contain different components there should be a difference in how easy water is worked into the grease matrix and this was also the case. Sample PP was surprisingly easy to mix with water and sample Ca-Min was very hard to mix.

As a first attempt at finding out if there are any differences in how water is accommodated inside the grease a comparison of infra-red spectra between the samples with and without water was performed. The result, which can be seen in *figure 15*, is a little surprising. There are large differences in how visible the water is in the IR-spectra, indicating that water probably is dissolved and/or emulsified differently in the samples.



**Figure 15:** Difference spectra between water free grease and sample with 10% water. The very broad peak shown belongs to symmetric and asymmetric stretching of the H-O-H bonds.

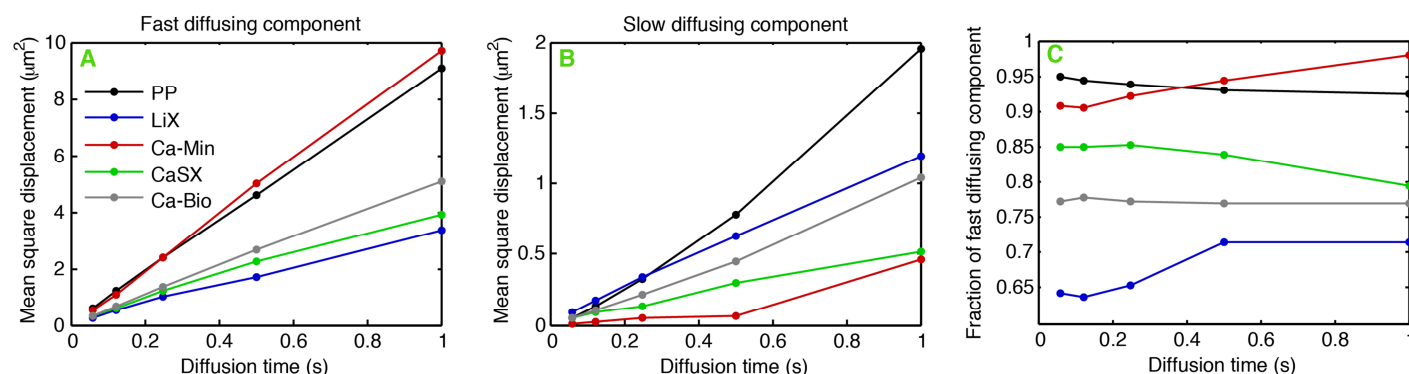


**Figure 16:** In a stable water-in-oil emulsion there are surface active components stabilising the reverse micelles (here represented by schematic detergent molecules). The water that is closest to the polar group of the surfactant will interact with the surfactant and therefore become restricted in its mobility (red dots in the figure). Water molecules further away will be less restricted (purple dots) and the water in the center of the reverse micelle will have a mobility closer to that of free bulk water. Smaller micelles have much less free water and therefore the self-diffusion constant of that water will be lower. The extreme of this would be a water molecule dissolved by itself in the oil-phase. This water molecule would diffuse slowest of them all.

To dig a little deeper into the question of how water is contained inside the greases we turn to diffusion NMR experiments. By the means of pulsed field gradient nuclear magnetic resonance (PFG-NMR) experiments it is possible to measure the self-diffusion coefficient of molecules – in this case water. Water can exist as free bulk water that only interacts with other water molecules or it can be restricted in its motion by interactions with

other molecules. Water molecules that interact so strongly with other molecules are sometimes referred to as bound water, but restricted water is probably a more accurate description.

The fact that larger reverse micelles have less water molecules that are restricted in their motion by interaction with surface active molecules results in that the self-diffusion coefficient for the water in larger micelles is greater than that of smaller micelles. By the use of PFG-NMR we can measure this self-diffusion coefficient and from this say something about the size and the distribution of micelles.



**Figure 17:** Panels A and B show the mean square displacement as a function of diffusion time for the fast diffusing component (larger water structures, panel A) and slow diffusing components (small water structures or dissolved water, panel B). Panel C illustrates the fraction of fast diffusing component.

The diffusion NMR experiments revealed two water populations in all samples: One fast diffusing and one slow diffusing. The fast diffusing population is interpreted as a water structure in the grease which contains water molecules which are less restricted in their movement, *i.e.* more similar to free water than the slow diffusing population. Still, the fast diffusing population had a diffusion constant which is two orders of magnitude slower than free bulk water [8]. The slow diffusing population can be either a much smaller water structures or water that is dissolved in the grease. Comparing the diffusion constant of the slow component to that of water dissolved in mineral oil, all values are in that range ( $0.8\text{--}1.5 \mu\text{m}^2\text{s}^{-1}$ ) [9].

The PP and Ca-Min greases contain the largest water structures of all samples and they contain very little or none of the slow diffusing population. The calcium sulphonate complex contains smaller water structures than greases PP and Ca-Min. There also seems to be quite some dissolved water in this grease (slow diffusing population). The interpretation of the result for the LiX sample is trickier. The sample contained the largest fraction of the slow diffusing component (dissolved water or small water inclusions) but there also seems to be some type of exchange between different water structures or between water structures and dissolved water as indicated by *figure 17 panel C*. The mechanism behind this exchange is unknown, but one can speculate that some type of “channel” is connecting the water structures. The Ca-Bio grease is also different from the other samples as it contains smaller fast diffusing water structures (similar to CaSX) but this sample also seems to contain quite a lot of dissolved water [10]. This higher level of dissolved water is most probably due to dissolved water in the esters that make up the base oil of this product.

How does this match up with the content of the tested samples? The Ca-Bio and the CaSX contain a lot of components which are potentially surface active. The fact that it is possible to create stable emulsions with more than 30% of water in the CaSX grease is a clear indication of this. The high concentration of surface active components makes it possible for smaller water structures to form. In the case of Ca-Bio we also have a base oil which probably has the capability to dissolve quite some water. The other samples contain larger bodies of water inclusion and these probably therefore contain less surface active components. An indication of this is that in these samples it was not possible to blend in more water than around 10% using a SpeedMixer. We also performed some tests with the PP sample where we tested a sample that was lacking the additives and this sample was significantly harder to mix water into and we could not reach 10% water inclusion. Further removing the tackifier in this grease resulted in a base grease into which it was impossible to mix any water at all. Thus, the ability of a grease to form stable emulsions with water seems to depend strongly on the availability of surface active components that originate mainly from the thickener and the additives.

## CONCLUSIONS

*Grease selection:* Based on the results from this study we can conclude that the choice that gives the best overall performance in wet environments is an anhydrous calcium soap thickened grease, preferably with a biodegradable (polar) base oil. If extreme pressure performance is needed or the operating temperature might become very high, an overbased calcium sulphonate complex is preferred. If the water is a process liquid containing high levels of emulsifiers a polymer thickened grease might be the best solution.

*Water in grease:* All greases contain, more or less, surface active components originating mainly from the thickener and the additives. The concentration and nature of these surface active components will determine how much water is possible to mix into the grease and form a stable water-in-oil emulsion. By carefully selecting the components of a grease it is therefore possible to control how much water a product can emulsify.

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