# THE FUNCTIONAL AND LONG TERM TEST OF ROUGE SENSOR, TYPE HPLG

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*Upon our request FORCE Technology (DK) has performed a series of tests with the HPLG rouge sensor in order to evaluate its function and long-term reliability which is described in this report [11 ].*

## Introduction

Rouging appears in the pharmaceutical industry where stainless steel equipment is exposed to hot purified water (PW), water for injection (WFI) or clean steam for extended periods. As a result, the internal surfaces become polluted by loosely adhered products and discoloured by oxide build-up. The precipitation of iron as fine red-brown ferric oxide or hydroxide particles is generally termed rouge due to the similarity with the cosmetic product "rouge".

Although rouging is common in systems for WFI and clean steam, the basic mechanism is still not fully understood. The available literature on rouging is limited and often suffers from misunder-standings related to the fundamental corrosion behaviour of stainless steel. WFI is sometimes characterized as a highly aggressive medium; likewise rouging is often associated with pitting or other destructive forms of corrosion. Both statements are highly questionable.

From our point of view rouging is a natural consequence of passive dissolution of stainless steel in systems having a large surface area and a high degree of recirculation. Although stainless steel is protected by a thin oxide film, a continuous and slow replacement of this film will always take place when exposed to wet conditions. Consequently, the alloying elements of the stainless steel are released to the media at a very slow rate. This rate can be influenced by parameters like surface finish, alloy type, flow rate and dissolved gases. In some WFI systems, rouging appears as quickly as a month or two after system start up. In other cases, it takes several years before rouging is observed.

Since there is no documented way to prevent the formation of rouge completely, common practice involves derouging of the WFI system at intervals ranging from a few months to several years in most pharmaceutical companies. For this purpose are used inorganic acids (passivation solution HC 1100) and/or chelating agents (stainless steel cleaner HC1106). Final passivation with nitric acid is recommended.

The main idea of the HPLG rouge sensor is to obtain in-line measurements of the development of rouge formation so that maintenance and derouging of the WFI system can be planned and verified with less need of system dismantling and visual inspections.


*HPLG instrument*

The basic principle of the concerned sensor implies measurement of the reflectance or luster of the stainless steel surface using a light source.

*HPLG sensor*

In our position as surface treatment and corrosion specialists, our knowledge of rouging is based on numerous inspections of pharmaceutical water systems and research projects on this phenomenon together with FORCE Technology.

Part of this work has been published in recognised journals and at international conferences [4,5,6,7,10].

# Experimental Procedures

1. **Functional Test**
2. **Long Term Test**

### Objective

The main objective of the performed tests has been to evaluate the function and reliability of the HPLG rouge sensor in a system producing rouge.

## 1. Functional Test

Two series of tests have been made; the first one to verify correct readings on four tube inserts in stagnant water, the second test to verify readings in circulating water at elevated temperature.

***Test 1 – Verification of Tube Inserts***

The rouge sensor was supplied with a test stand and four tube inserts that allow verification of the operation. The tube inserts numbered 1 to 4 represent four degrees of rouging as shown in ***Figure 1*** :

1. No rouging
2. Little rouging
3. Moderate rouging
4. Pronounced rouging


***Figure 1***
*Tube inserts representing different degrees of rouging. The tubes measure: 162 x 21.8 x 1.5 mm (length x outer diameter x wall thickness)*

Each tube insert was tested in double at ambient temperature (22℃) using the test stand as shown in ***Figure 2***.

Prior to testing, the tube insert was carefully placed in the cell so that the opening faced the sensor.

Subsequently, the cell was filled with deionised water having a specific conductivity of less than 0.8 µS/cm at 25℃.

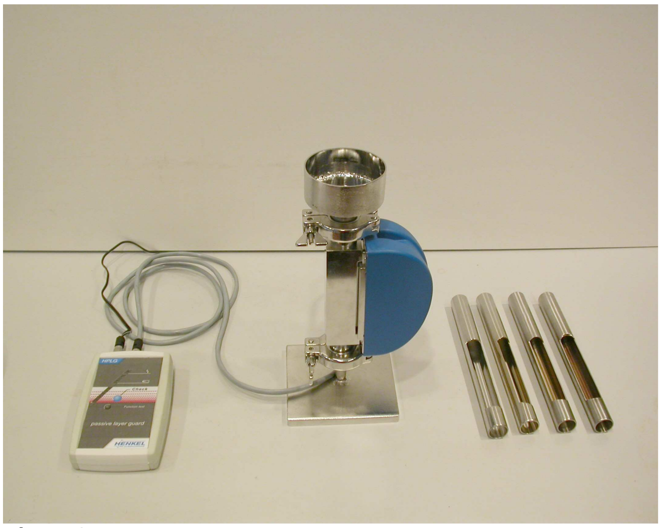

***Figure 2***
*Test stand supplied with the instrument for measurements in stagnant water*

The instrument was allowed to warm-up for at least five minutes before measurement.

Readings were then made by pressing the Check and Function Test button simultaneously for about 1 second until the Measurement LED started flashing, ***Figure 3***.

When the Measurement LED gave a constant signal (after 10 seconds), the degree of rouging was read on the LED meter.

The conductivity of the water was measured in all tests using a Radio-meter pIONeer 65 instrument.

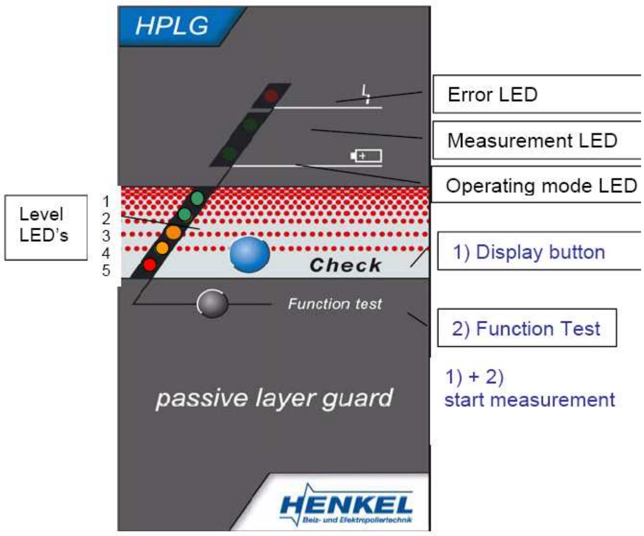


***Figure 3***
*Display and function buttons on the HPLG instrument*

*Test 2 – Readings in Circulating Water at Elevated Temperature*

In order to test the sensor under conditions close to those occurring in WFI systems, a small circulation loop was build. The set-up consists of a thermostat with a circulation pump loop connected to the cell with silicone hoses. In order to avoid trapping of air-bubbles, which might affect the measurement, the cell was tilted slightly. A picture of the complete test set-up is shown in ***Figure 4***.

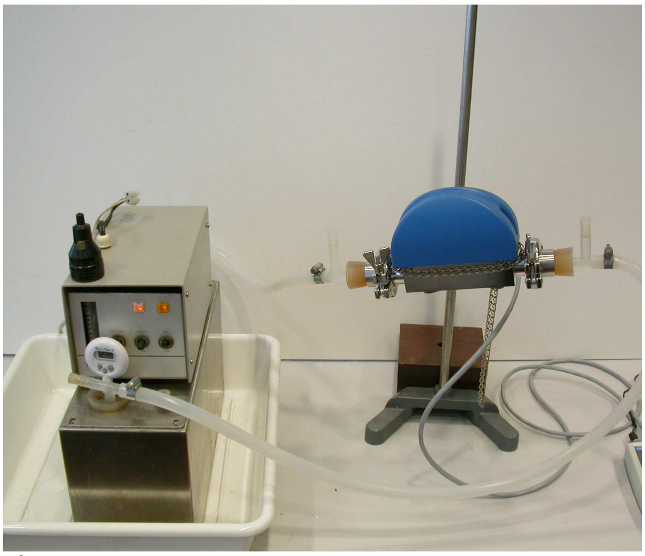

***Figure 4***
*Overview of set-up used for circulating water at different temperatures*

Prior to each test the tube insert was carefully placed in the cell so that the opening faced the sensor.

The system was then filled with deionised water having a specific conductivity of less than 0.8 µS/cm. The conductivity was verified using a Radiometer pIONeer 65 instrument.

The HPLG instrument was allowed to warm-up for at least five minutes before first reading and it remained switched-on throughout the entire test cycle. Each test involved heating from 20°C to 80°C in steps while maintaining constant circulation (5 litre/min ≈ 0.3 m/sec). The degree of rouging was read several times at each temperature according to the procedure above. Typically, each test cycle lasted for 3 hours.

All tube inserts were tested in double using this procedure.

## Results (Functional Test)

The instrument gives readings within one unit of the corresponding tube inserts. This means that the reading of Tube No. 1 shall be 1±1, the reading of Tube No 2 shall be 2±1 etc. Our evaluation of the tests is based on this criterion.

### *Test 1 – Verification of Tube Inserts*

By using the supplied test stand and tube inserts the following readings were obtained with the HPLG instrument, **Table 1**.

**Table 1 -** Results of tests in stagnant water at ambient temperature.

| Insert | Conductivity, µS/cm (test1/test2) | Readings (test1/test2) | Result |
|---|---|---|---|
| Tube 1 | 0.59 / 0.24 | 1, 1, 1 / 1, 1 | Pass |
| Tube 2 | 0.59 / 0.24 | 2, 2 / 2, 2 | Pass |
| Tube 3 | 0.59 / 0.24 | 3, 3 / 3, 3 | Pass |
| Tube 4 | 0.59 / 0.24 | 3, 3, 3, 3 / 4, 4 | Pass* |

*) Deviation is within specified precision

Since the principle of the measurement is dependent on the in-build light source, readings were taken both with and without covering the tube insert.

The circumstance had no effect on the readings, which means that daylight from surroundings has no influence on the obtained reading of the tube insert in the test stand. In all cases, the obtained readings were within the specified precision of the instrument.

### *Test 2 – Readings in Circulating Water at Elevated Temperature*

The results of eight tests in circulating water at different temperatures are shown in **Table 2**.

**Table 2 -** Results of tests in flowing water at different temperatures.

| Insert | Conductivity, µS/cm (test1/test2) | Temperature | Readings (test1/test2) | Result |
|---|---|---|---|---|
| Tube 1 | 0.53 / 0.74 | 20℃ | 1, 1 / 1, 1 | Pass |
| | | 40℃ | 1, 1 / 1, 1 | Pass |
| | | 60℃ | 1, 1 / 1, 1 | Pass |
| | | 80℃ | 1, 1, 1 / 1, 1 | Pass |
| Tube 2 | 0.72 / 0.71 | 20℃ | 2, 2 / 2, 2 | Pass |
| | | 40℃ | 2, 2 / 2, 2 | Pass |
| | | 60℃ | 2, 2 / 2, 2 | Pass |
| | | 80℃ | 2, 2, 2 / 3, 3 | Pass* |
| Tube 3 | 0.53 / 0.53 | 20℃ | 3, 3 / 3 | Pass |
| | | 40℃ | 3, 3 / 3, 3 | Pass |
| | | 60℃ | 3, 3 / 3, 3 | Pass |
| | | 80℃ | 3, 3, 3 / 3, 3, 3 | Pass |
| Tube 4 | 0.51 / 0.53 | 20℃ | 4, 4 / 4, 4 | Pass |
| | | 40℃ | 4, 4 / 4, 4 | Pass |
| | | 60℃ | 4 / 4, 4 | Pass |
| | | 80℃ | 4, 4 / 4, 4 | Pass |

*) Deviation is within specified precision

It clearly appears that the water temperature has no influence on the reading of the instrument.

In one case (Tube 2 at 80℃) the instrument indicated a slightly higher degree of rouging than expected, but the result is still within the specified precision.

The tests prove that the HPLG instrument gives consistent readings that reflect the degree of rouging well at conditions relevant to WFI systems.

## 2. Long Term Test

Two approaches have been applied to simulate such conditions, the first one using a stainless steel loop circulated with WFI for long time, the second one based on rouge generated by dissolution of iron (artificial rouge formation).

***Test 1 – WFI loop***

The HPLG rouge sensor was supplied with a test loop that allows heating and circulation of water, ***Figure 5***. Basically, the circulation system consists of a water tank (material 1.4435/316L) with heating, a pump, over-pressure valve and a conductivity probe; all connected with stainless steel piping (material 1.4435/316L). The HPLG rouge sensor is placed as shown in the photo to avoid collection of gas bubbles on the sensor and the opposite surface.

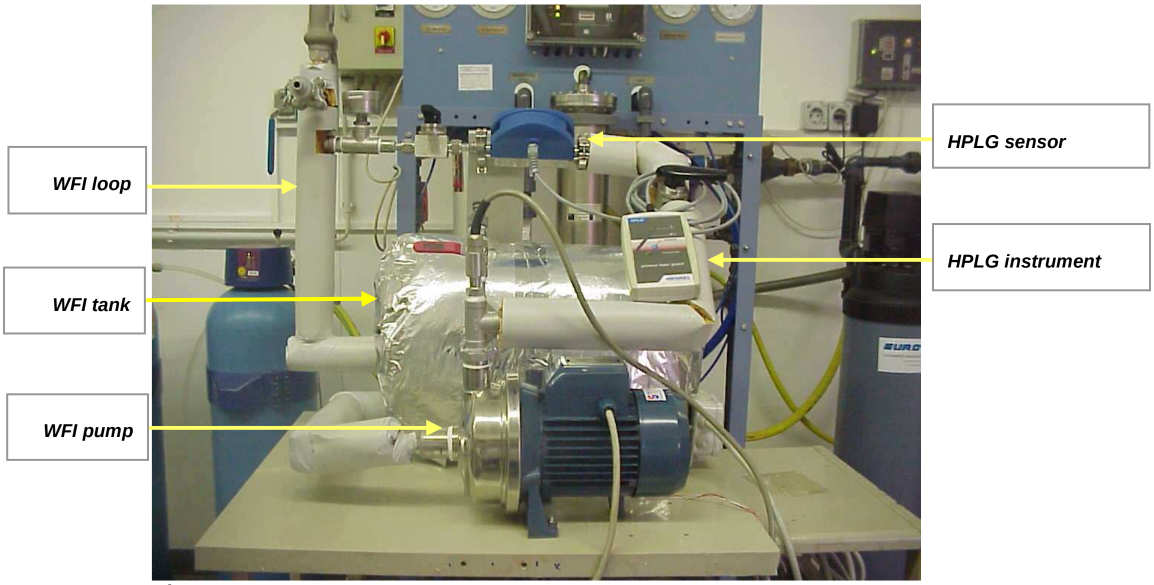


***Figure 5***
*Overview of WFI loop used for the long-term tests*

WFI from a pharmaceutical plant was used for filling the system. The water and loop were purged with nitrogen prior to filling. Afterwards, the temperature was raised to 95-100℃ and kept there for the entire test period while circulating the water. The entire system contains approximately 25 litres.

Throughout the test, the temperature and conductivity were monitored with the in-line sensor using datalogger equipment. Readings with the HPLG rouge sensor were made manually at least three times a week.

After the test, the sensor-cell was evaluated visually and by "wiping" to characterise the degree of rouging. Examination was also made with a video endoscope.

### *Test 2 – Artificial rouge formation*

In order to let the sensor test strong rouge formation in the WFI loop up to level 5 another set-up was established to produce rouge more rapidly. The set-up consists of a heated cell that also contains a small iron anode that can be dissolved galvanically. The cell is connected to a circulation pump loop and the HPLG rouge sensor by use of silicone hoses. Removable pieces of stainless steel pipe (ø22 mm) are also inserted in this loop for sampling during the test. In order to avoid trapping of air-bubbles, which might affect the measurement, the cell was tilted in both set-ups. A photo of the complete test set-up is shown in ***Figure 6***.

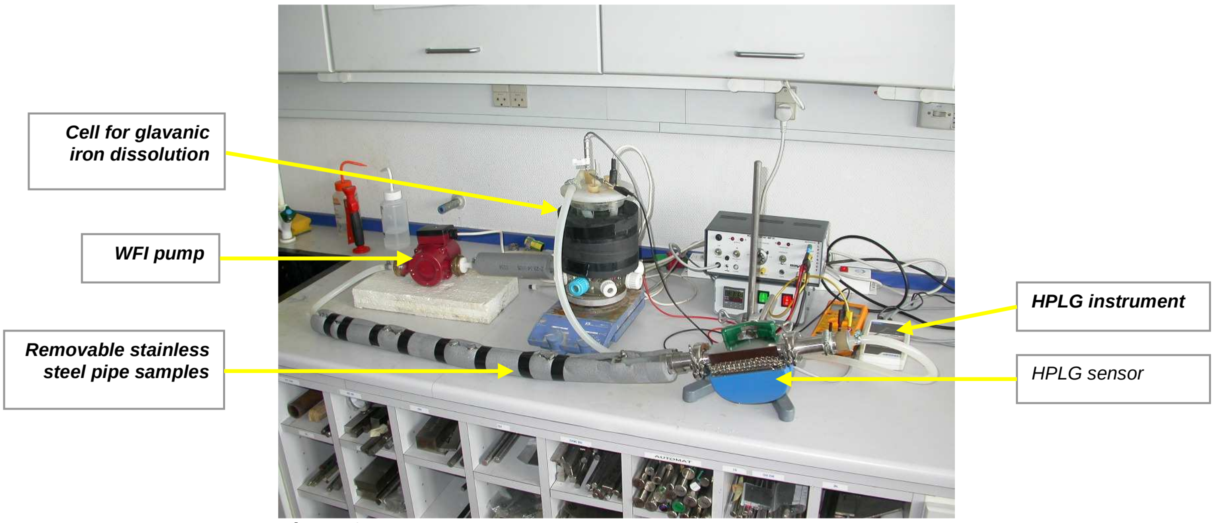


***Figure 6***
*Overview of set-up used for artificial rouge generation*

Deionised water having a specific conductivity of 1 µS/cm was used for the test. The water was heated to 80℃ while maintaining constant circulation (5 litre/min ~ 0.3 m/sec). In order to generate rouge the iron was dissolved galvanically at a current density of 0,5 - 2 $mA/cm^2$ over 2 - 4 days in the daytime.

Readings of the temperature and the HPLG rouge sensor were taken manually at hourly intervals. When a change in the rouge level was observed, one of the stainless steel pipes was removed from the loop.

Several tests were made using the second approach with artificial rouge formation. Prior to each test, the HPLG rouge sensor was cleaned using an ethanol soaked wipe mounted on a bottle-rinser to reset the reading level.

After the test, the pipe samples were sectioned length-wise for visual evaluation to characterise the degree of rouging. The rouge sensor was evaluated visually too.

## Results (Long Term Test)

***Test 1 – WFI Loop***

Two tests were carried out by using the supplied WFI loop.

The first test lasted 47 days. The development in temperature and conductivity was monitored. The temperature was fairly constant at 96℃ while a slight increase in conductivity was observed, presumably, gas bubbles in the system interfered the conductivity measurements.

Throughout the test, no change was observed in the readings of the HPLG rouge sensor, which at all times showed the lowest level (1). Visual inspection and wipe-test of the surfaces inside the sensor showed no signs of rouge in agreement with the readings. However, traces of grey products could be collected with a cotton stick, but from the limited amount we would not expect a response from the HPLG rouge sensor.

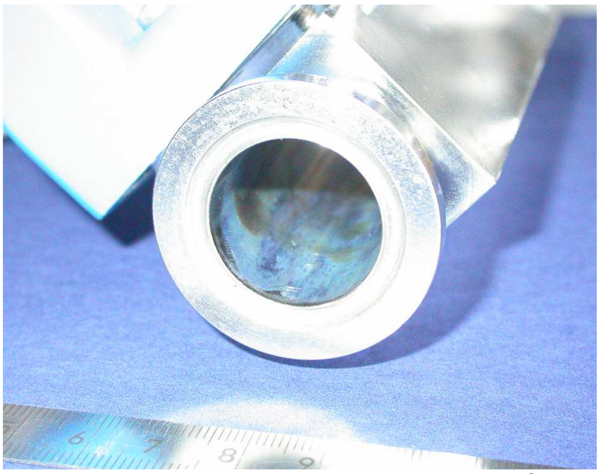


***Figure 7***
*Slight rouging inside the HPLG cell after 80 days exposure in the WFI loop. The surface appears "milky" with a few red-brown areas*

The second test lasted 80 days same monitoring of temperature and conductivity. The rouge sensor initially showed level 1, which changed to level 2 while heating the water from 20 to 98℃. After 52 days the level 3 LED started to flash, which indicates an increase in rouge level. The new level 3 was confirmed by pressing the check button. No further change was observed for the remaining 28 days of the test.

Visual inspection of the surfaces inside the sensor showed slight discoloration. The surface appeared “milky” with a few red brown spots at the inlet end of cell, ***Figure 7***. Endoscopy was also attempted for examination, but this technique did not prove useful for characterising small colour changes. Finally the cell was cleaned with an ethanol soaked wipe. Only colourless deposits were collected by this. However, the cleaning removed all surface deposits and reset the sensor to level 1.

In summary the two long-term tests demonstrate that the HPLG rouge sensor responds well to small changes in rouging or discoloration of the stainless steel surface within the cell. Moreover, the instrument has shown good overall long-term stability without any signs of functional problems.

### *Test 2 – Artificial rouge formation*

Due to the limited rouge formation in WFI loop, it was decided to perform a series of tests where rouge was generated artificially.

Different attempts were made, essentially using the same set-up as shown in ***Figure 6***.

The first attempt of dosing ferro sulphate to water circulating at 80° C did not prove successful.

Galvanic dissolution of pure iron turned out to give better similarity with rouging by showing both loose products and build-up of adherent oxide-layers on the stainless steel, ***Figures 8 + 9***.

The HPLG rouge sensor and removable pieces of stainless steel pipe were exposed in the same loop at 80℃ in circulating water over several days while slowly dissolving iron.

A pipe sample was removed when a change in the rouge level on the HPLG rouge sensor was observed. The test was continued until level 5 was obtained.

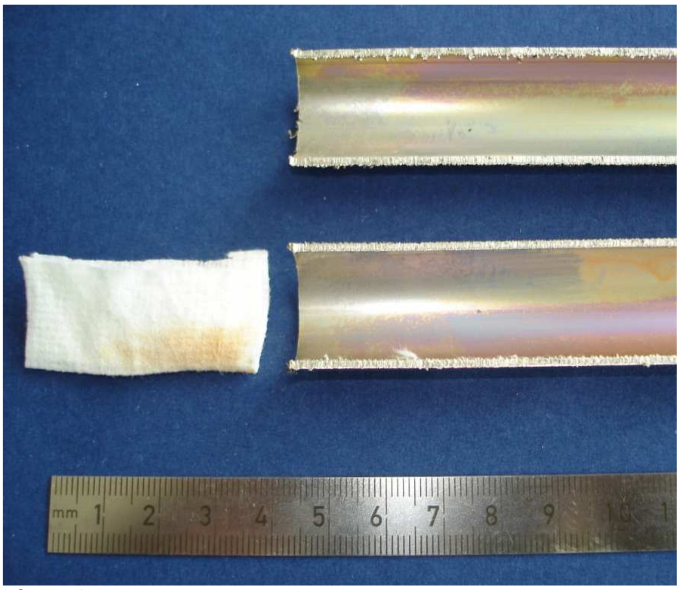

***Figure 8***
*Loosely adhered rouge and oxide build-up in a stainless steel pipe after galvanic dissolution of iron*

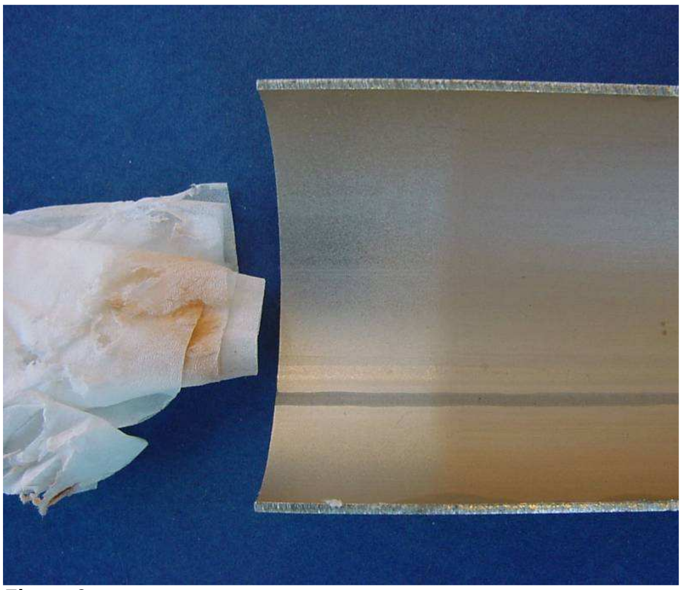

***Figure 9***
*Loosely adhered rouge particles in a pipe from a full-scale WFI loop (80℃) in a pharmaceutical plant. The pipe measures 2½" in diameter*

The subsequent examination of the sectioned pipe samples showed a clear difference in the degree of rouging in good correlation with the readings on the HPLG rouge sensor, ***Figure 10***.

Levels 3 and 4 correspond with slight discoloration of the surface whereas level 5 involves presence of loose particles as well.

The observations on the pipe samples correlated well with the appearance of HPLG cell after the test, ***Figure 11***.

Loose particles could be wiped off the surface that showed discolouration too.

The tests with artificial rouge formation prove that the HPLG instrument gives consistent readings that reflect the degree of rouging well at conditions relevant to WFI systems.

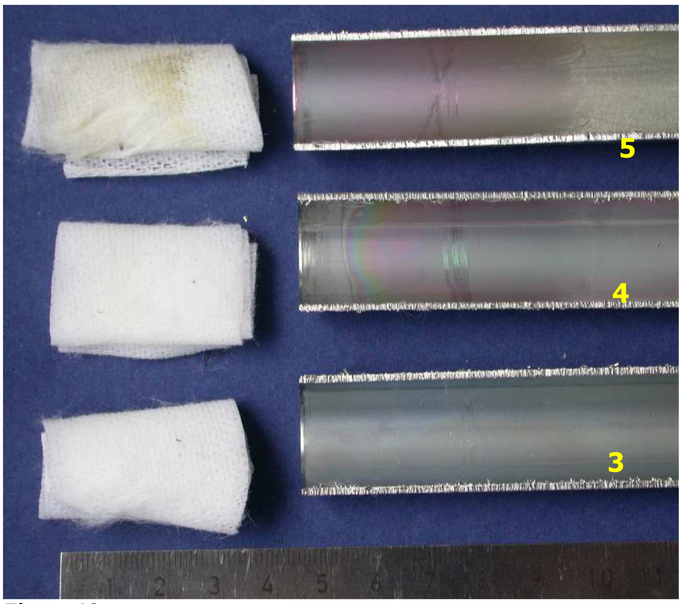


***Figure 10***
*Sectioned pipe samples removed from the loop with artificial rouge generation at readings from 3 to 5 on the HPLG instrument. The high reading (5) corresponds well with the presence of loose particles collected by the wipe*

***Figure 11***
*Rouging inside the HPLG cell after the test involving artificial rouge formation. Loose particles may be wiped off the surface*

# Discussion

The above tests have been performed in a way that simulates rouging in a WFI loop as closely as possible.

## 1. Functional Test

The tested inserts represent the form of rouging that is related to thickening of the protective oxide layer on the stainless steel. In most cases, this behaviour will subsequently lead to formation of loosely adhered rouge particles, which involve a risk of product contamination.

Since the deposition of rouge particles affects the reflectance even more than oxide build-up on the surface, we find it very likely that the HPLG instrument will respond effectively to such changes too.

In 2 out of 40 tests the readings of the instrument deviated one unit from the expected level of the insert. This behaviour was only observed with the discoloured inserts (No. 2 and No. 4) whereas the clean insert (No. 1) always showed the expected level. Moreover, the results are in all cases within the specified precision, which still enables an early detection of critical rouge formation in the WFI system.

## 2. Long Term Test

While the first tests were solely based on tube inserts that represented the form of rouging related to thickening of the protective oxide layer on the stainless steel, the long term tests involved longer exposure times showed much greater similarity to those conditions found in full scale WFI loops.

In the current tests the effect of particulate matter has been simulated as well by dissolving iron galvanically. Whereas the formation of coloured oxide films on stainless steel may be ignored in a pharmaceutical production, the risk of particulate contamination cannot be ignored. Consequently, we find it very important that the instrument is capable of responding to this form of rouging as illustrated in ***Figures 8 and 9***.

The test with artificial rouge formation was capable of simulating both types of rouging. As it appears from the removed pipe samples, the stainless steel surface is firstly discoloured by oxide build-up at readings from level 2 to level 4 on the instrument. Finally, the particulate deposits are also observed on the surface of the stainless steel, which corresponds with the maximum level (5) on the instrument. This scenario is very similar to the typical development of rouging in a full scale WFI system. We base this on experience from inspections in a large number of WFI and clean steam systems [10].

The long-term tests with the small WFI loop did not develop rouge to a critical level within the exposure time of 45 and 80 days. This was somewhat expectable from the experience in full size WFI systems. Still, these tests have verified that the HPLG rouge sensor responds well to small changes in rouging and provide good long-term stability without any signs of functional problems.

The possibility of detecting changes in the oxide layer as well as deposition of particles is considered a strong tool for scheduling and validating derouging (cleaning) and re-passivation operations in a WFI system. The performed tests prove that the HPLG rouge sensor is capable of detecting such changes, even at a very early stage.

Besides advantages related to planning and validation of derouging and re-passivation operations, we see other possibilities with the new instrument. As mentioned, the mechanism and parameters that influence on rouging are poorly understood today. By undertaking on-line measurements, the rouge development can be quantified and correlated to service conditions and events in WFI systems. This way, decisive factors may be identified allowing adjustments to the system. Given this possibility, the tendency to rouging may possibly be minimised and thereby extend the intervals of derouging and re-passivation.

# Conclusion

The function and reliability of the HPLG rouge sensor has been tested by FORCE Technology (DK) in the laboratory under conditions comparable to those occurring in WFI systems.

## 1. Functional Test

Rouging was simulated using tube inserts representing four different degrees of rouging. Testing was made in both stagnant and flowing water having a conductivity of less than 0.8 µS/cm at temperatures between 20℃ and 80℃.

In all cases the sensor gave readings that corresponded to the degree of rouging of the tube insert.

Consequently, the rouge sensor was found applicable for in-line detection of rouging in WFI systems.

## 2. Long Term Test

The tests have involved long-term exposure (up to 80 days) in a small WFI loop with circulating water at 80° C. Only limited rouge formation was ob served in these tests which demonstrate that the HPLG rouge sensor responds well to small changes in rouging or discoloration. Moreover, the instrument has shown good overall long-term stability without any signs of functional problems.

In order to test the full rating scale of the HPLG rouge sensor, a second series of tests was performed, which involved artificial rouge formation by galvanic dissolution of iron. In all cases the sensor showed readings with good correlation to the obtained degree of rouging that was assessed by evaluating exposed tube pieces from the same loop.

Based on this, the rouge sensor was found applicable for in-line detection of rouging in WFI systems. This possibility may in many cases reduce the need for system dismantling and visual inspections that otherwise are required to plan and verify derouging and re-passivation of the WFI-systems.

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