MACO-PILOT

Sensor material corrosion investigations and sensor lifetime estimation

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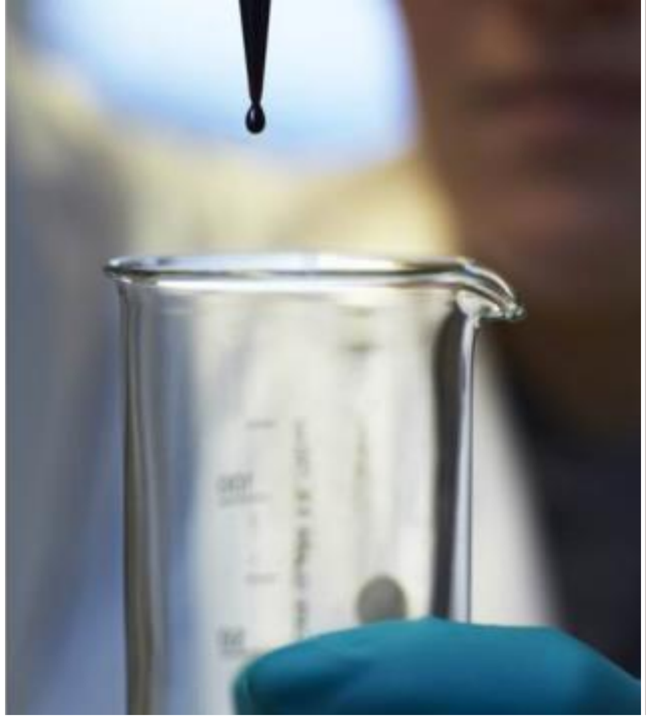
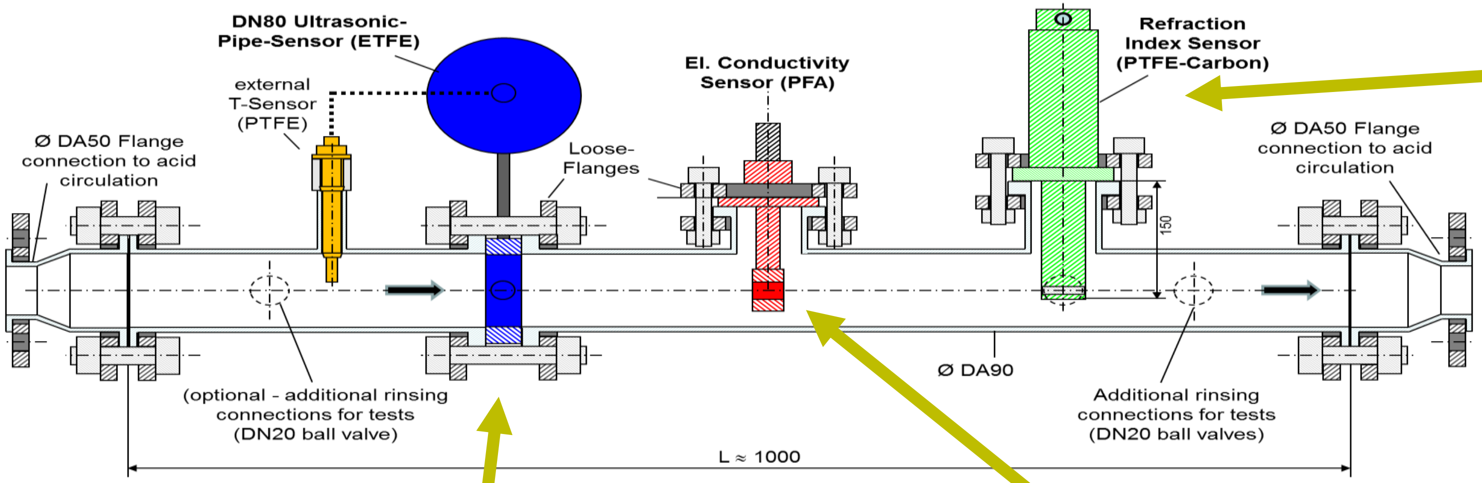
November 2019

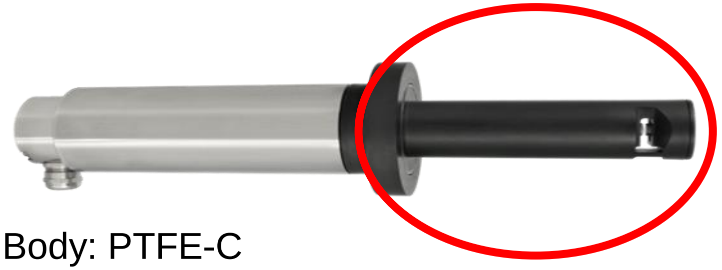
RISE Research Institutes of Sweden

DIVISION
ENHET



MACO Pilot





Body: PTFE-C
Packing: FFKM
Lens: Sapphire glass

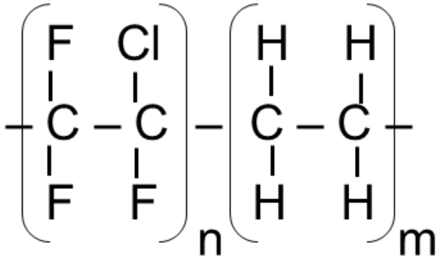
Body: EFTE coated steel
Temp sensor: PTFE

Body: PFA coated steel
Flange: PTFA

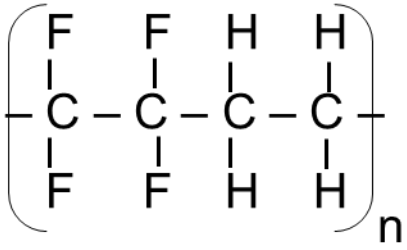
Fluoroplastics

- Have very good chemical and thermal resistance
- They are divided into fully fluorinated and partially fluorinated fluoroplastics
- Teflon is the most commonly know fluoroplastic (PTFE)
- The fluoroplastics are not degraded by the mixed acid used for stainless steel pickling

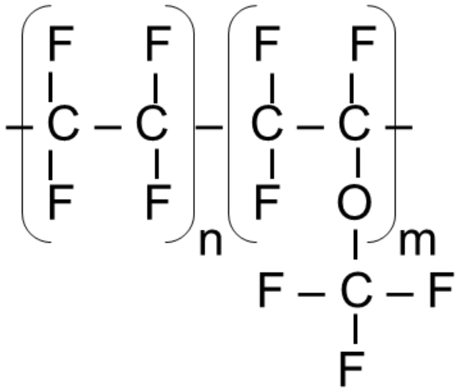
- ECTFE



- EFTE



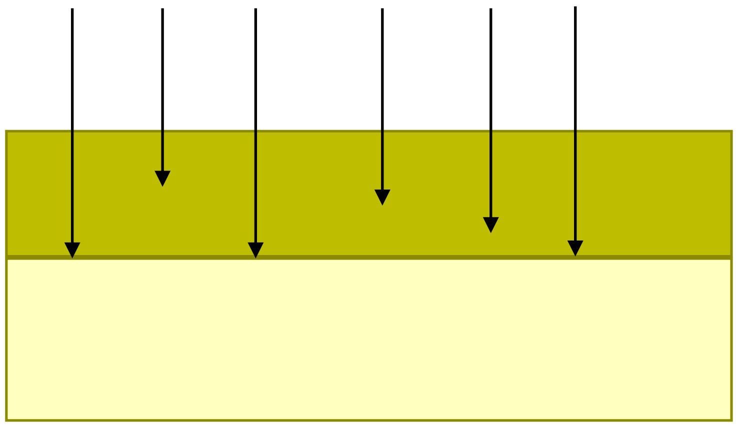
- PFA



HOWEVER…

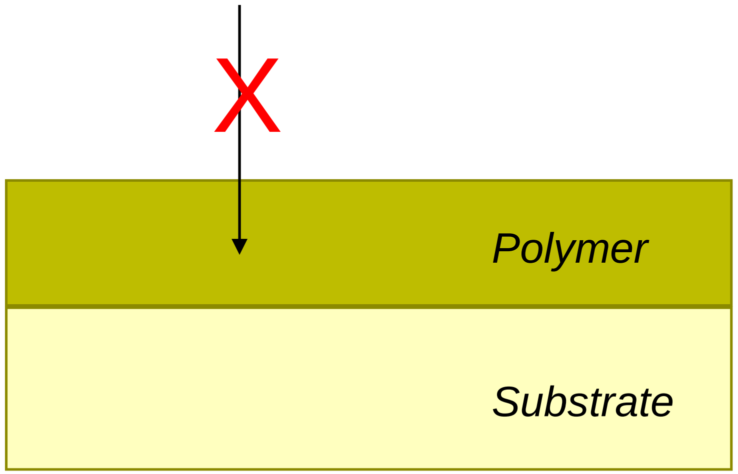
Plastics are permeable to small molecules

O_2, HF, HNO_3, NO_x, H_2O



Ions do not permeate into the polymer

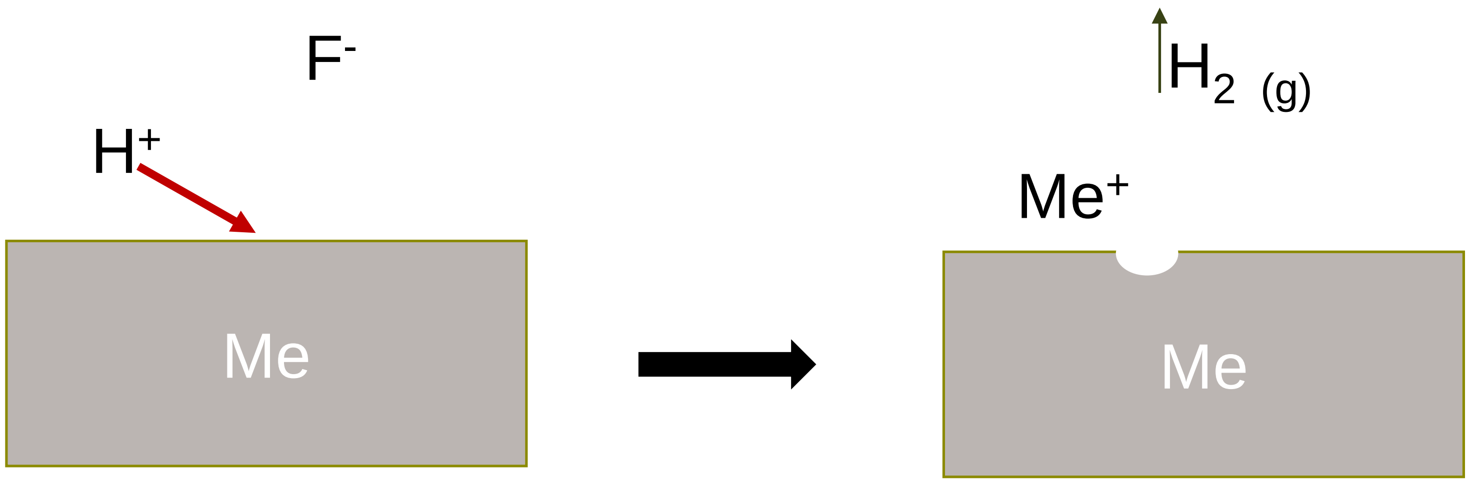
F^-, H^+



This diffusion is quite fast but the solubility is normally very low in fluoroplastics

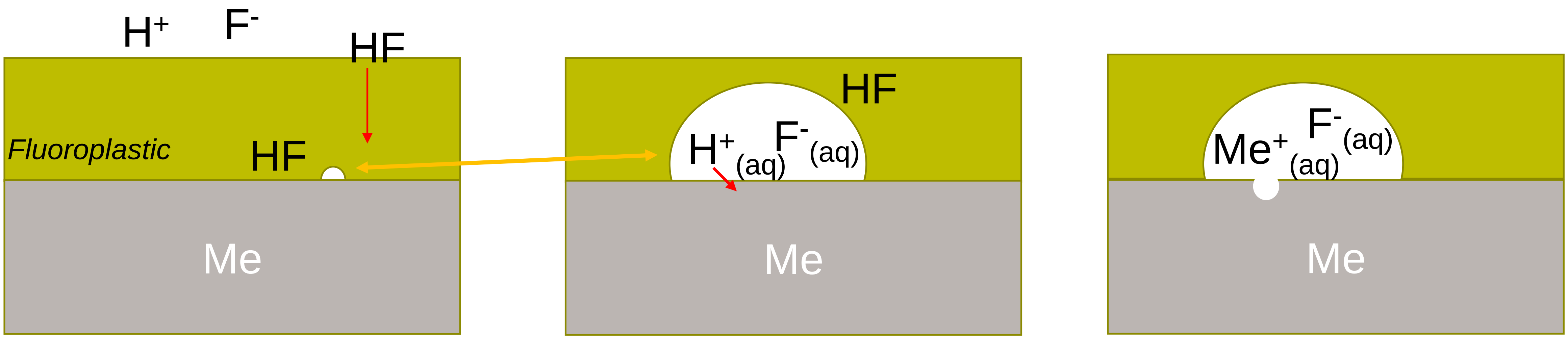
Corrosion of metals in acids

$$\text{Ex: } 2\text{Me} + 2\text{H}^{+} \rightarrow \text{Me}^{2+} + \text{H}_2$$

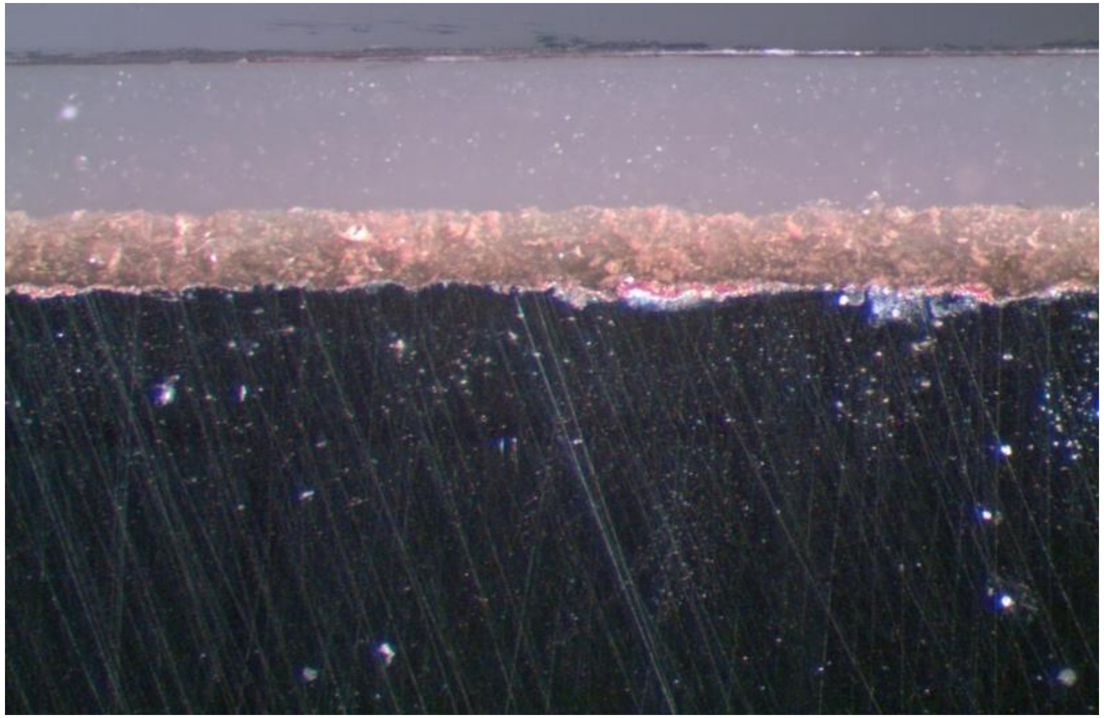


With imperfect polymeric coating

Only the molecular form of the acid (HF) diffuse through the polymer (together with water)
An imperfection in the coating could cause dissociation of the acid and subsequent attack on the metal



Polymer coatings



- The steel needs to be pre-treated to optimise the adhesion of the primer layer
- The primer must be optimised to have good adhesion to the steel and the polymer
- The polymer has to be modified to allow for application on the substrate
- This is different from normal polymer processing

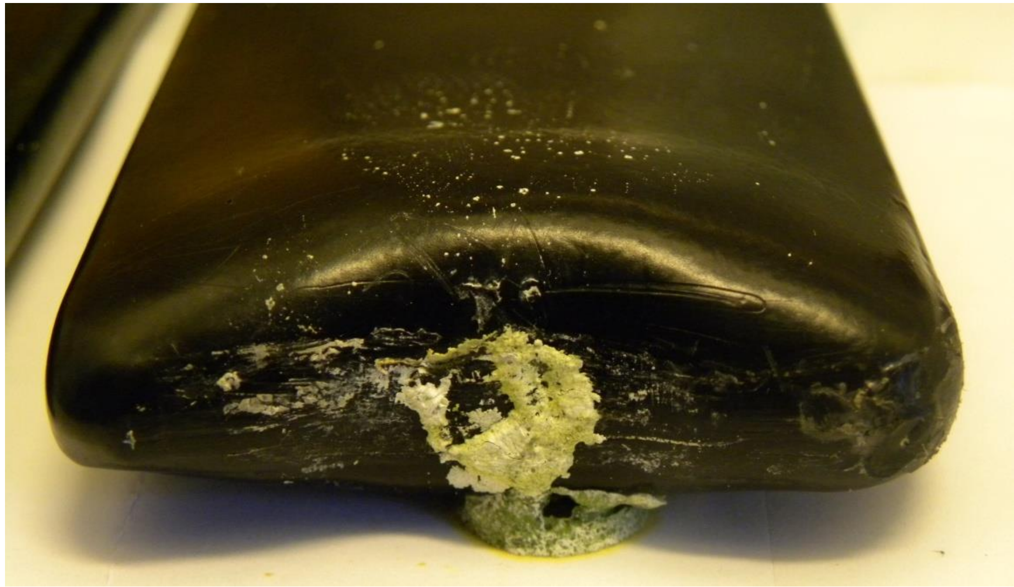
What happens when the penetrating acids reaches the interface between the steel and the coating?

- Unless there is a void large enough to create a liquid water phase in which acids can dissociate there is probably no risk of corrosion of the steel
- How well the coating sticks to the steel is thus very important
- But what is the failure criteria for a coating?
- How long would it take from a delamination to a corrosion that is changing the function of the sensor?

After appr. 3 years in service (mixed acid 65^{0}C)
1 mm ECTEF coating

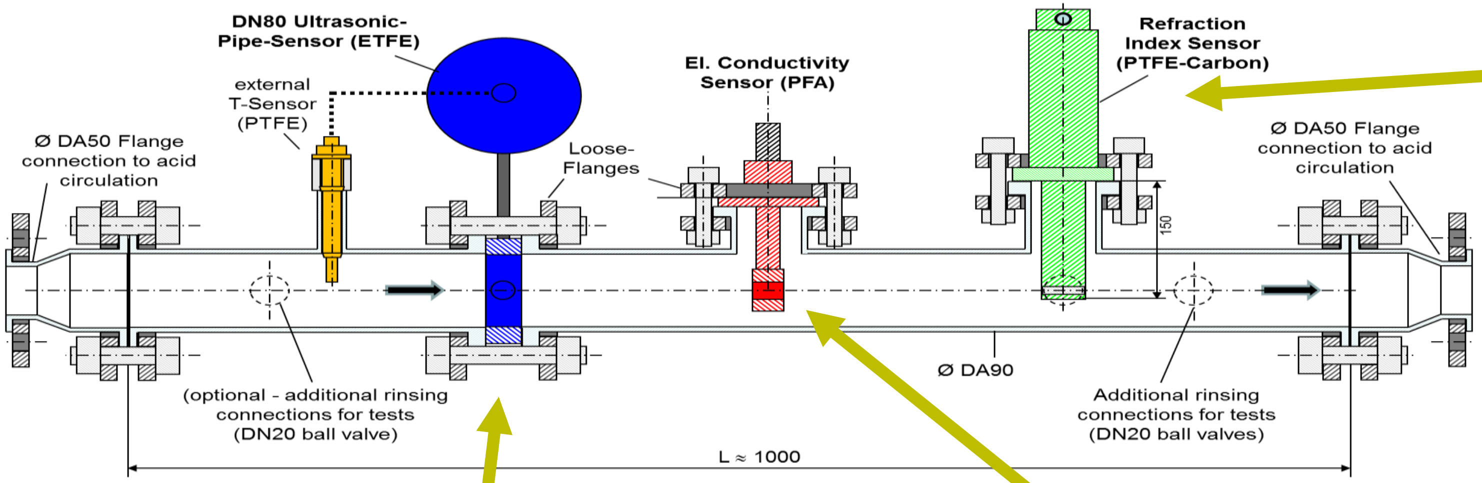
Another sensor with the same coating had a lifetime of 5.5 years

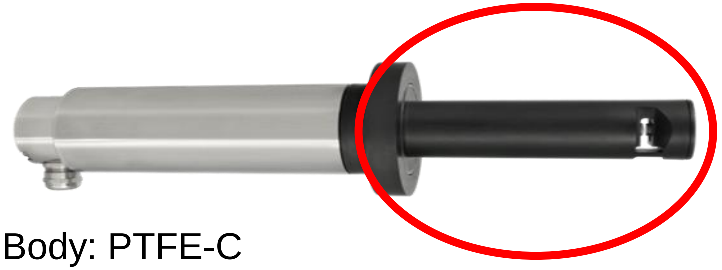
One major difficulty in exposing coated samples to study the diffusion is that there is a risk of penetration through holes in the coating. In this example at the point where it was hanging during the coating process



Task 4.3:

- **Investigations with new and operationally applied sensors of the installed mixed acid online concentration measuring systems**





Body: PTFE-C
Packing: FFKM
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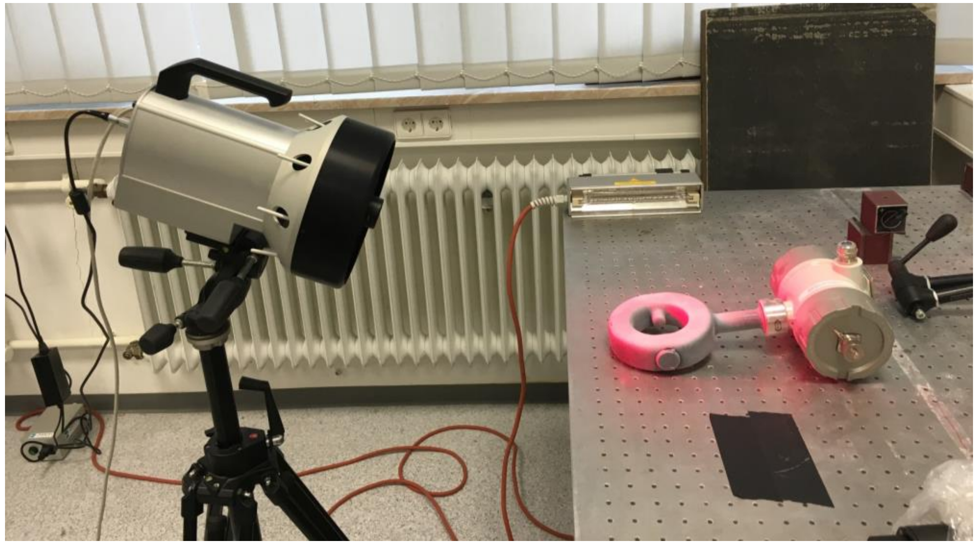
Body: EFTE coated steel
Temp sensor: PTFE

Body: PFA coated steel
Flange: PTFA

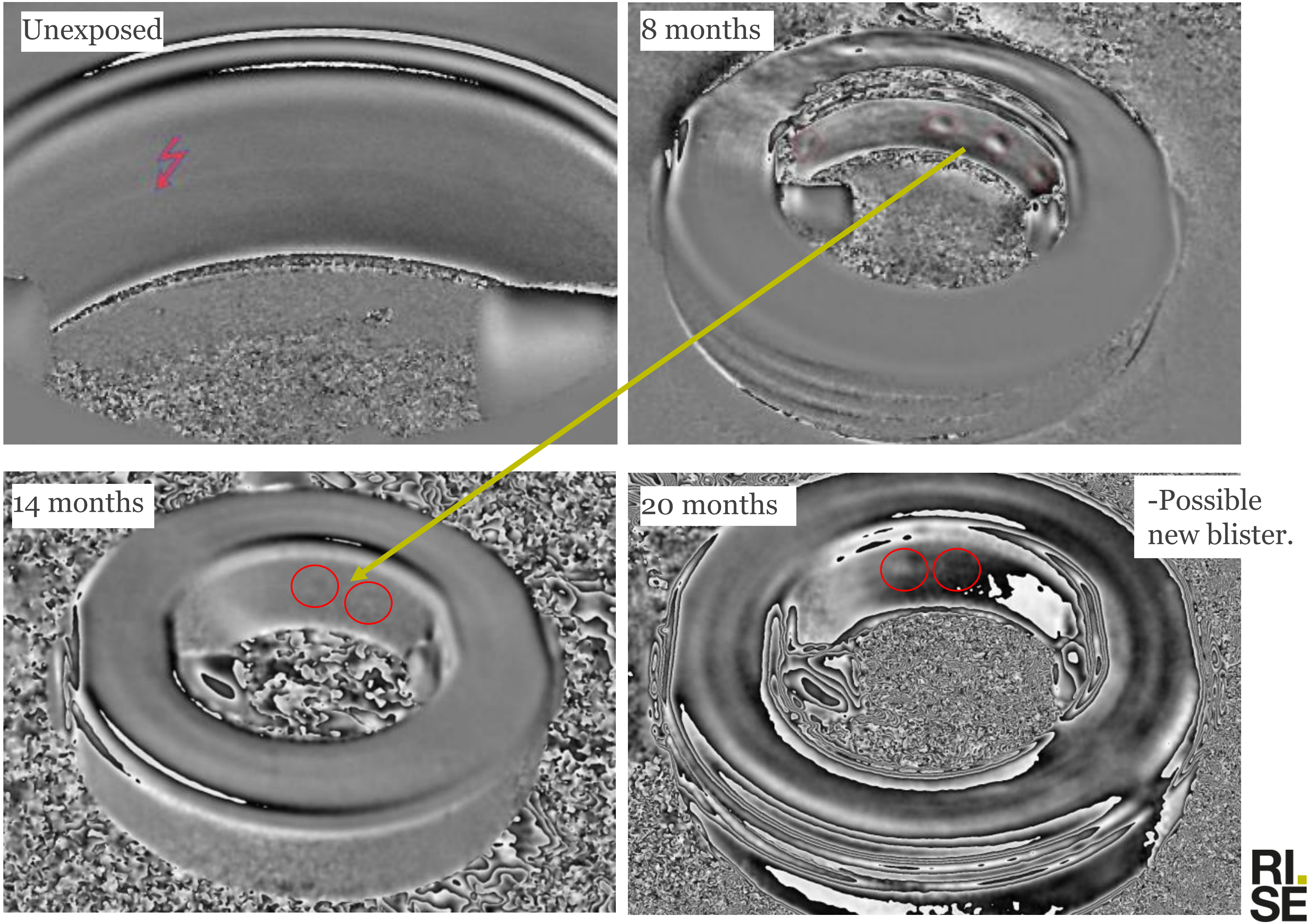
- Four sensor packs have been installed at four on-site locations.

- All US-sensors were analyzed with LASER Shearography prior to installment

- The status of the US-sensor are followed by regular analyzes LASER Shearography.

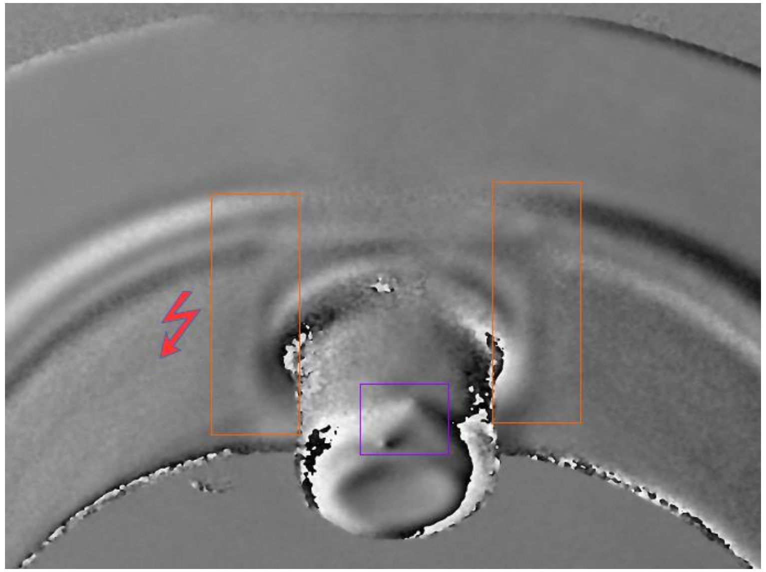


Pickling line, sensor 1

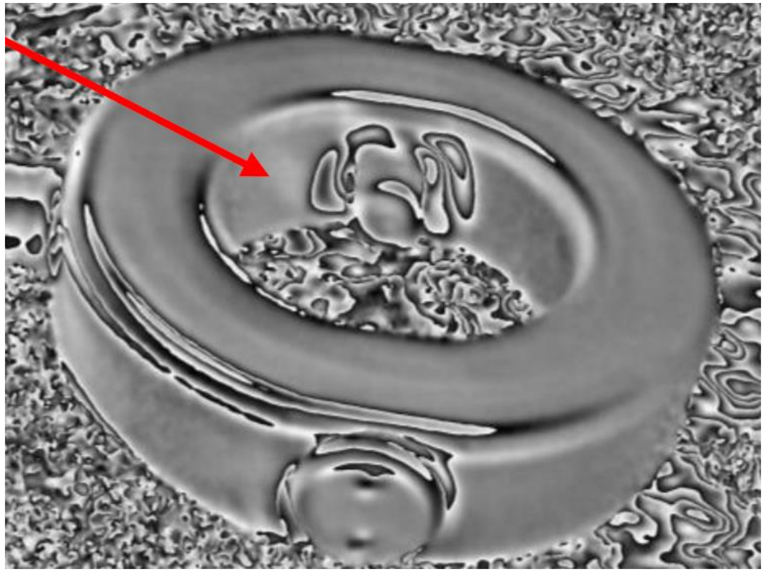


Sensor 2 exposed in pickling line

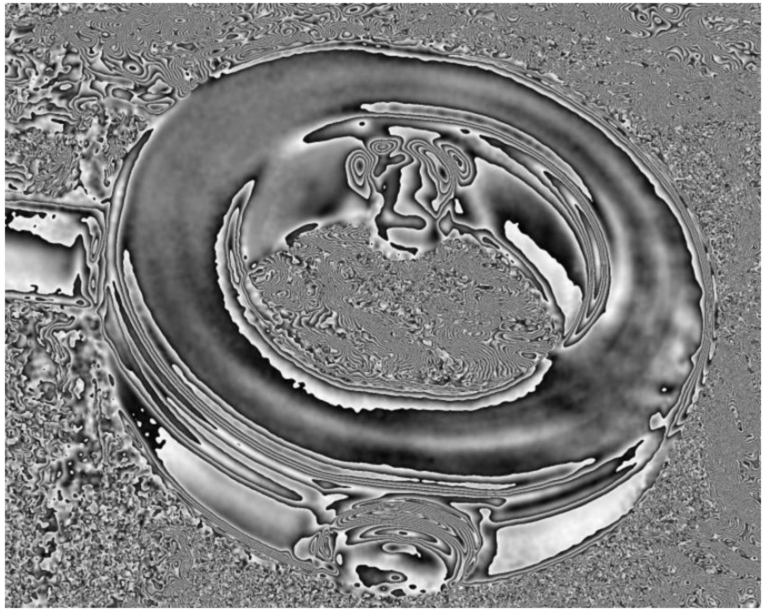
Unexposed



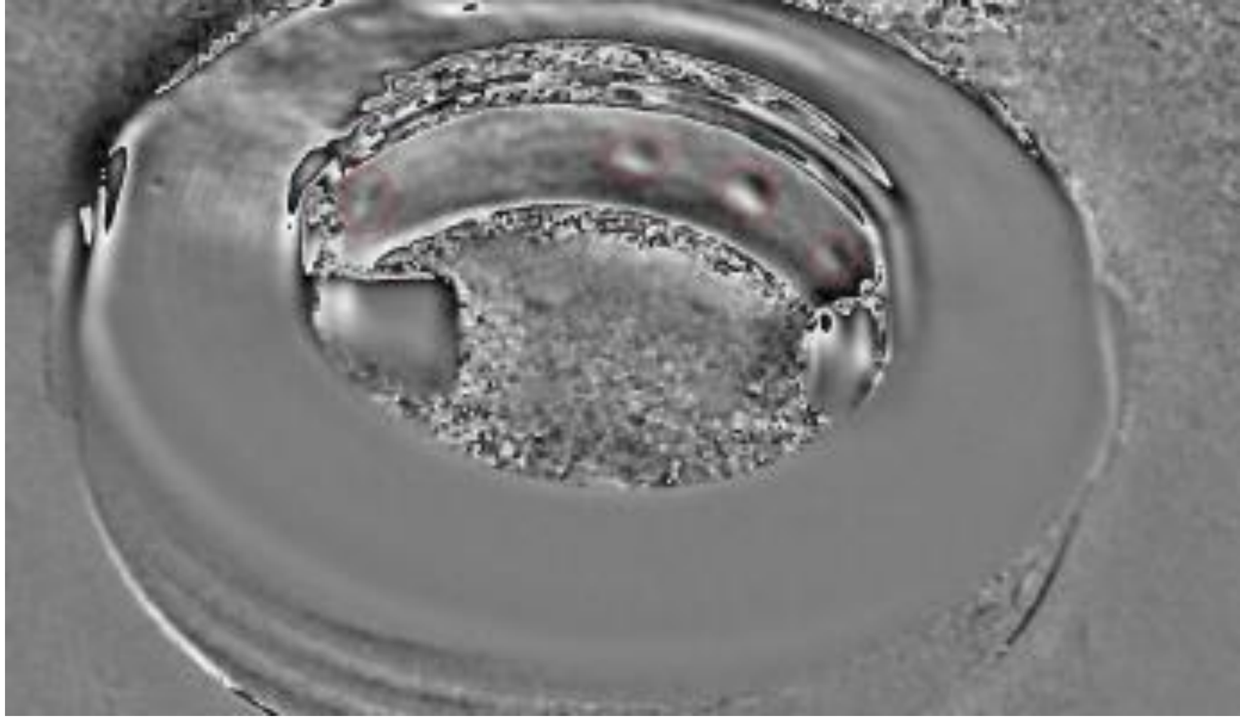
14 months
-possible delamination around head.

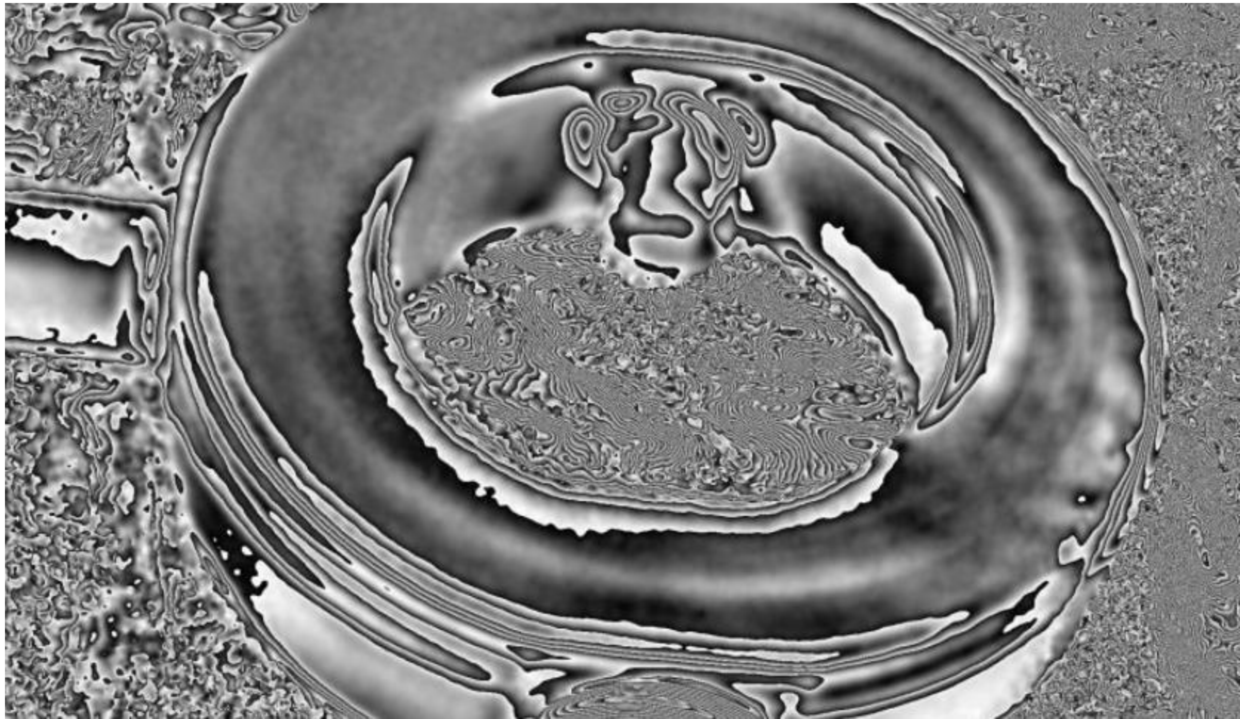


20 months
-possible growth of delamination around head.



- What is acceptable?
- What affects the function of the sensor?





Electrical conductivity sensor

- Moulded into PFA with a top of PTFE
- No corrosion can be found under the thick PFA coating (ca 5 mm)
- Corrosion in the area where the PFA meets the PTFE
- They can be separated fairly easily from each other
- Was solved by moving the joint further away from the acid.

Task 4.2:

- **Long-term laboratory material corrosion investigations of sensor material specimens for enhanced online sensor lifetime**

Development of exposure technique

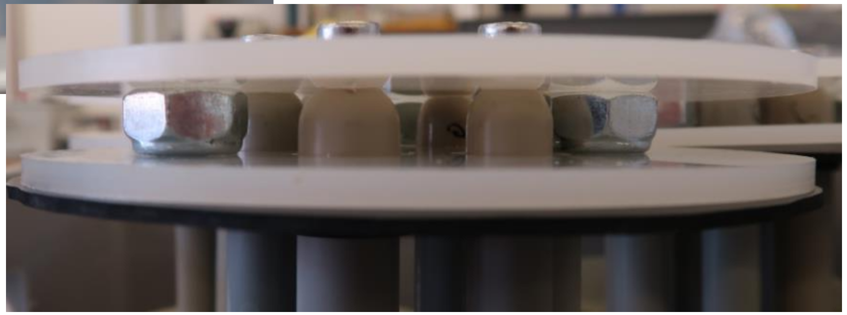
- An important part of the project has been to develop a method to expose steel samples with polymeric coatings
- As the samples are coated, they need to be attached to something, which is why a fully coated samples is difficult and therefore a traditional immersion testing is out of the question.

Evolution of exposure containers

- Initially the pins were attached to the lid. This allowed the threading to be above the liquid, but it was still in contact with the gaseus phase.

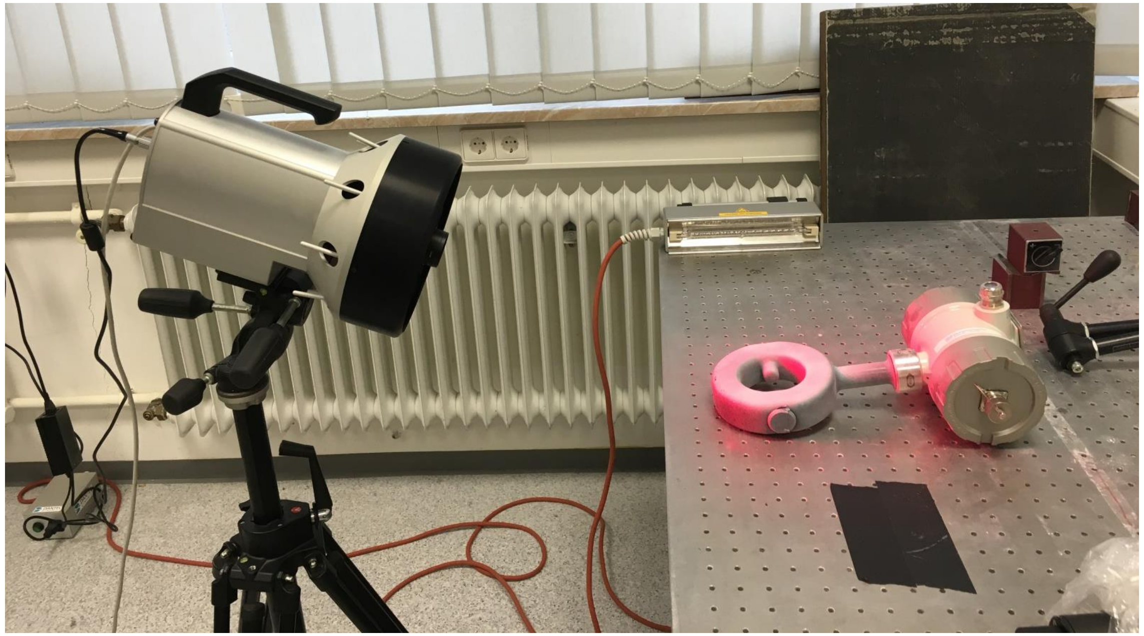
- By constructing a double lid, where the bottom layer seal the jar so it retains the acid, and the top layer is taking the load, a successfull design was achieved.

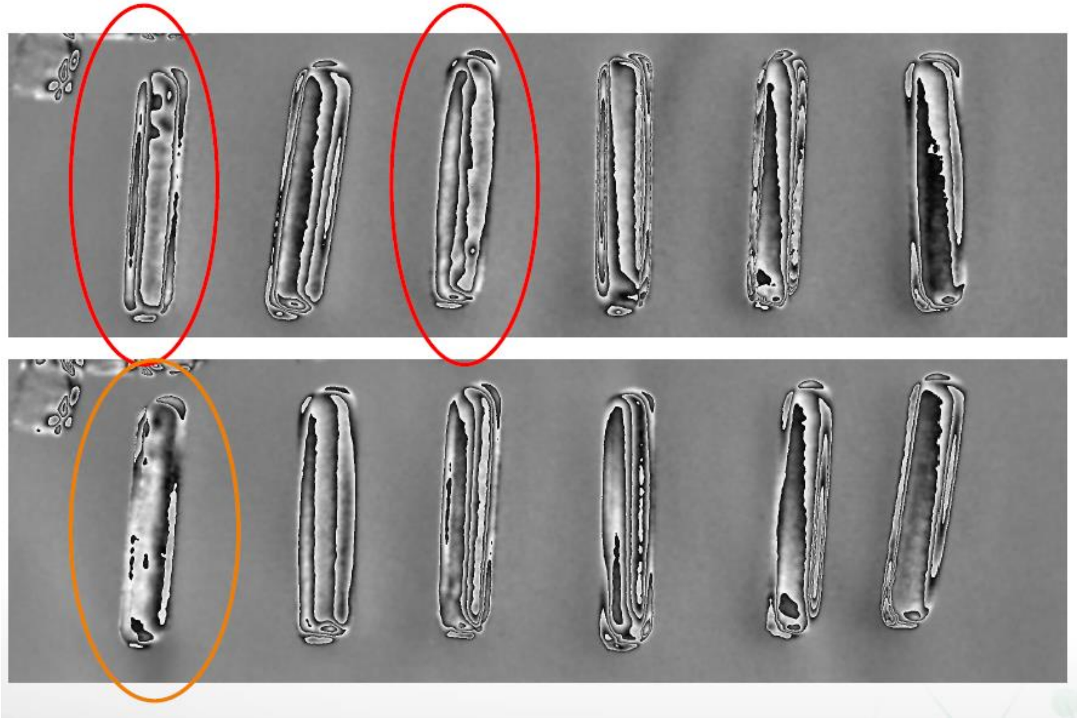
  If acid were to escape from the sealing layer, there is a ”ventilation crevice” between the layer, to prevent the acid from entering the threading.



Investigation of exposed pins

- 192 pins have been exposed
- LASER Shearography indicated delamination of varying degree on 30 pins (16%)

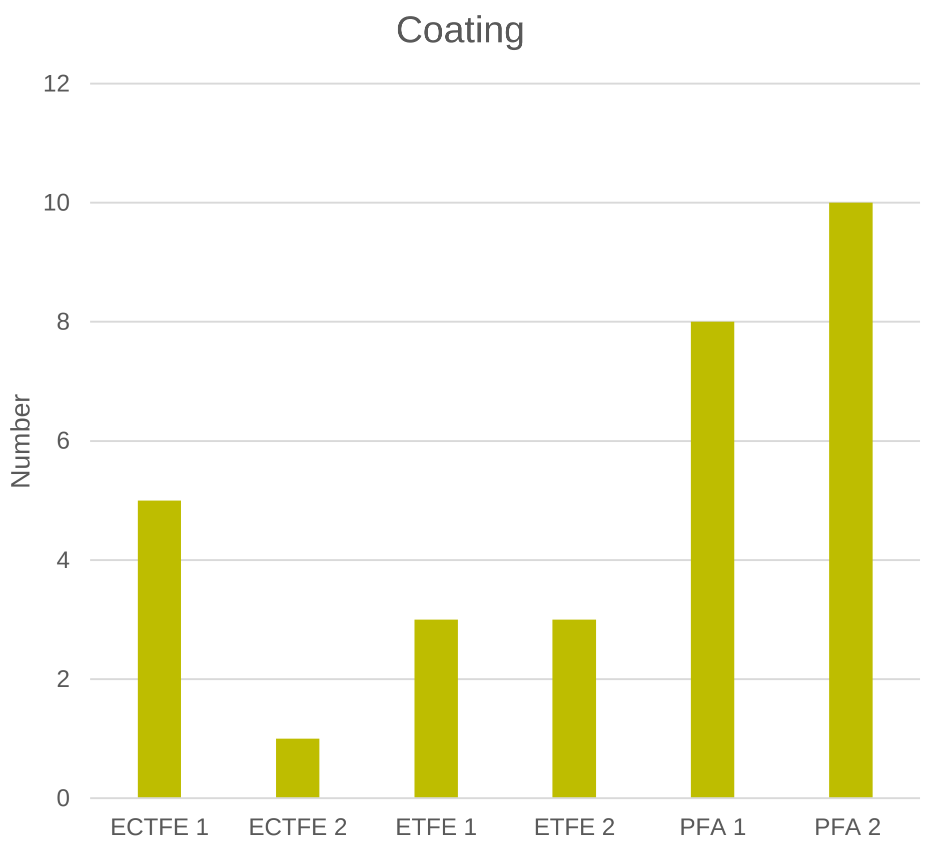




Distribution of the delaminated pins - Coating

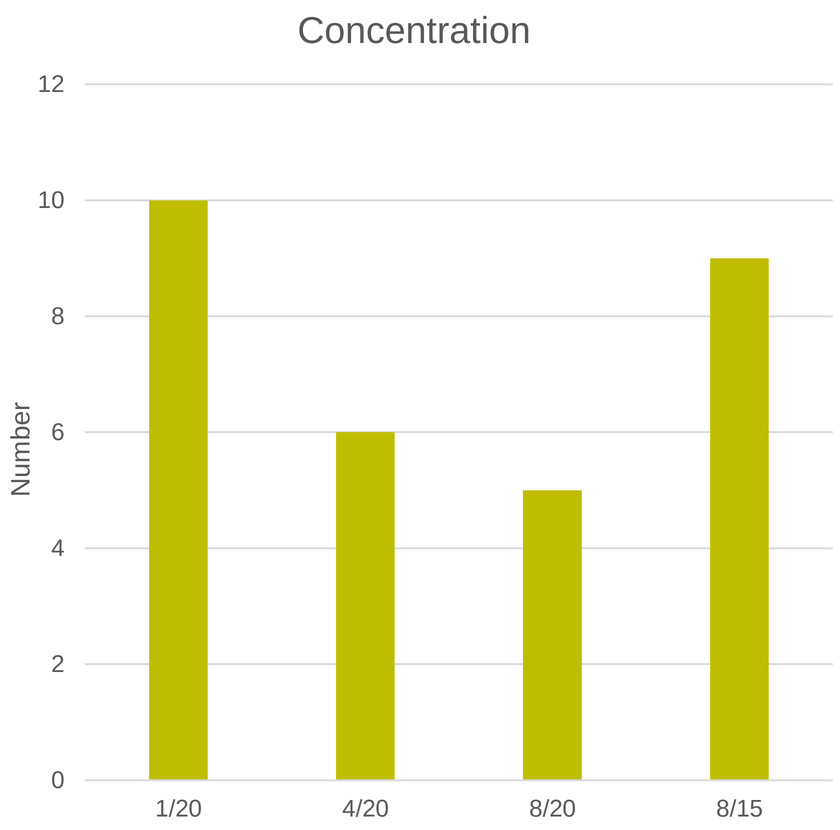
- 6/30 (20%) ECTFE
- 6/30 (20%) ETFE
- 18/30 (60%) PFA

- 16/30 (53%) 1 mm
- 14/30 (47%) 2 mm



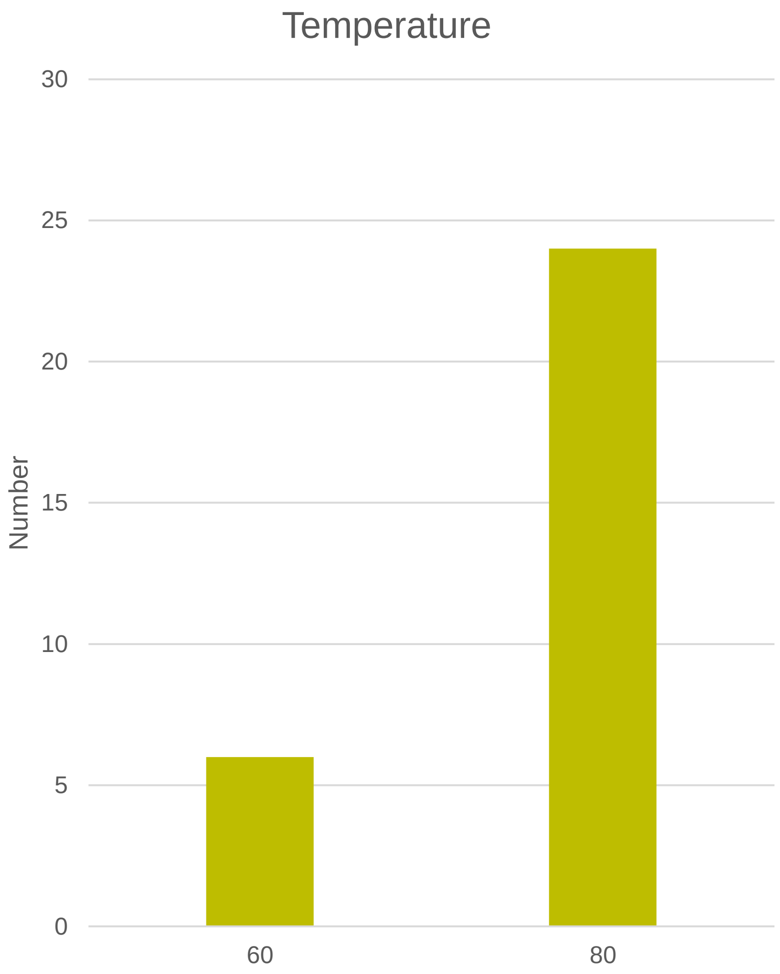
Distribution of the delaminated pins - Concentration

- 10/30 (33%) 1/20 HF/HNO3
- 6/30 (20%) 4/20 HF/HNO3
- 5/30 (17%) 8/20 HF/HNO3
- 9/30 (30%) 8/15 HF/HNO3



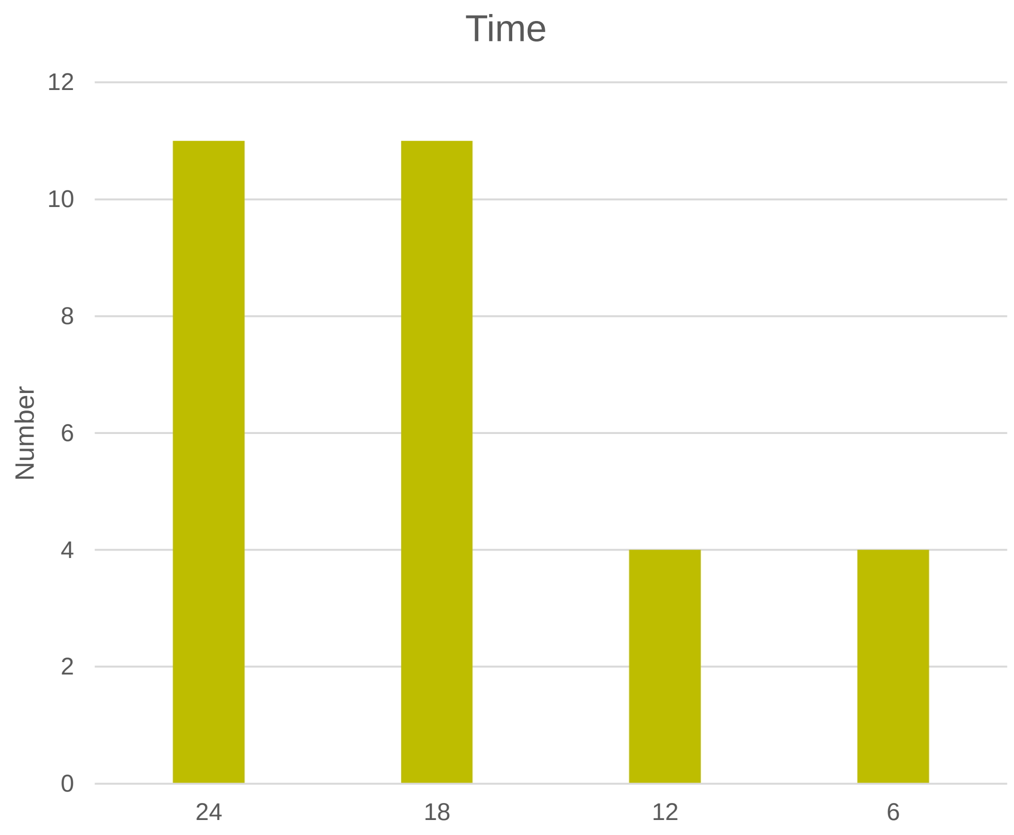
Distribution of the delaminated pins - Temperature

- 6/30 (20%) in 60^0C
- 24/30 (80%) in 80^0C



Distribution of the delaminated pins - Time

- 11/30 (37%) 24 months
- 11/30 (37%) 18 months
- 4/30 (13%) 12 months
- 4/30 (13%) 6 months

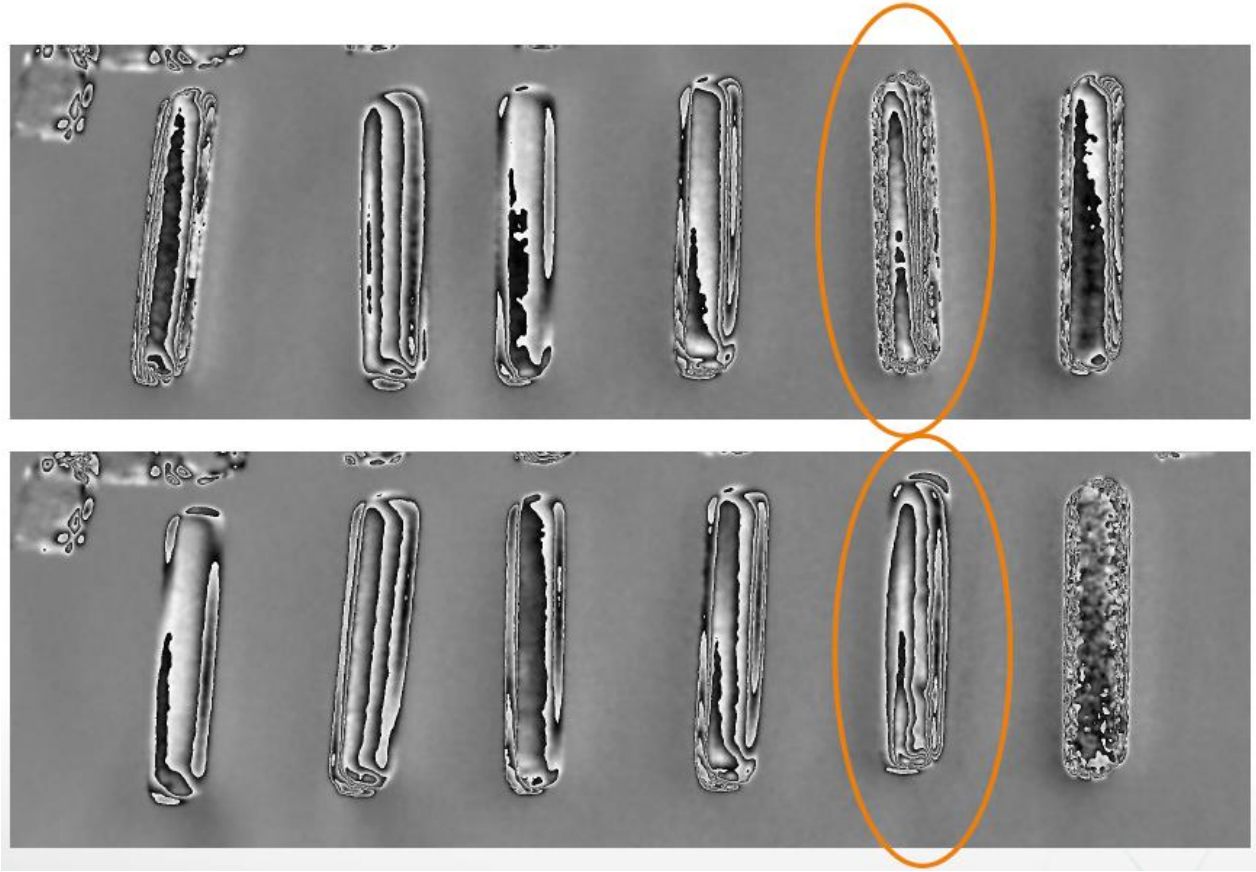


Validating LS – Jar 28

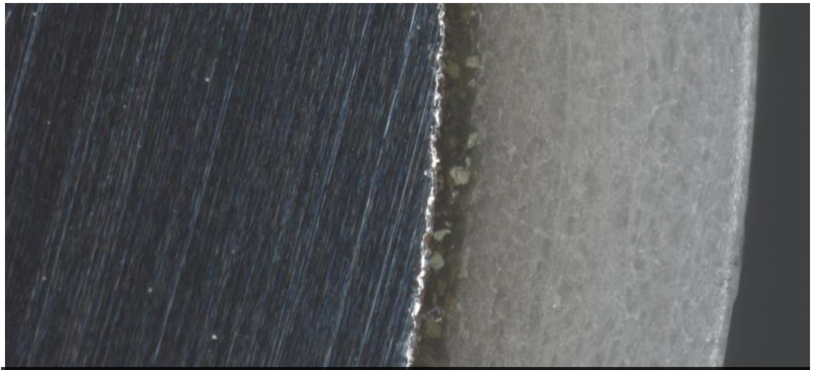
- 8/15
- 60ºC
- 6 months

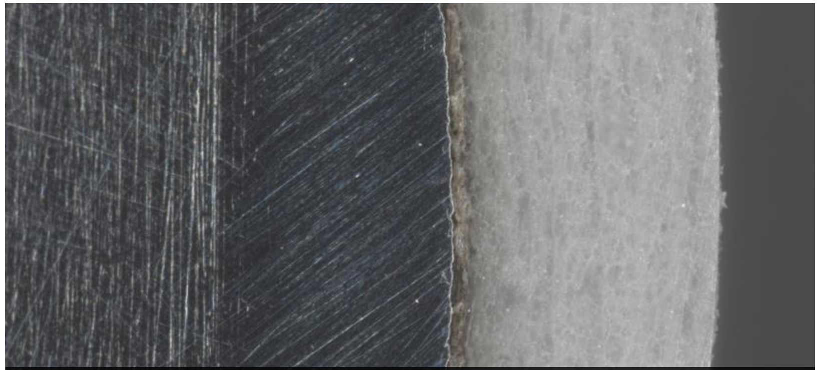
- LS indicated only one delamination:

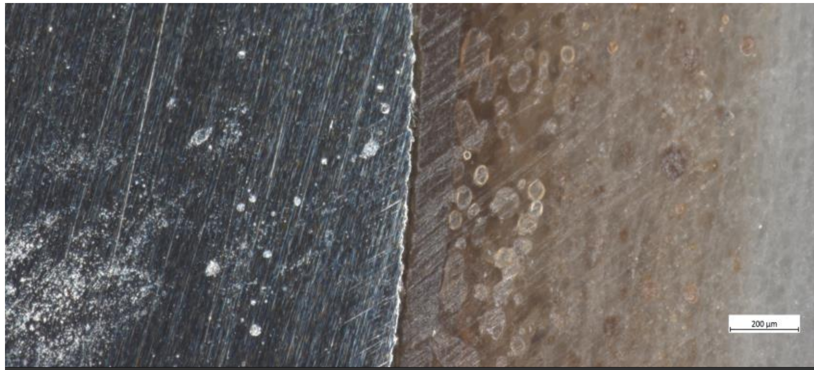
  28-5 (PFA 1 mm)

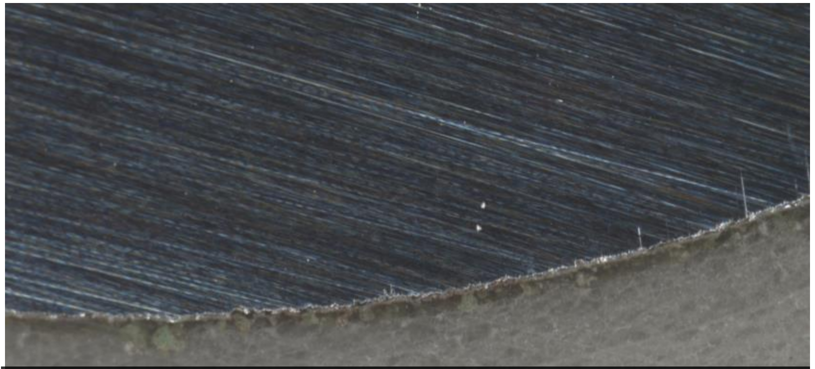


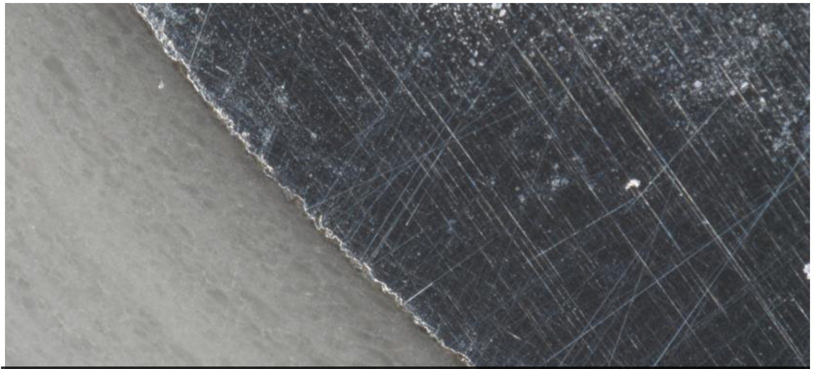
Cross sections of Jar 28

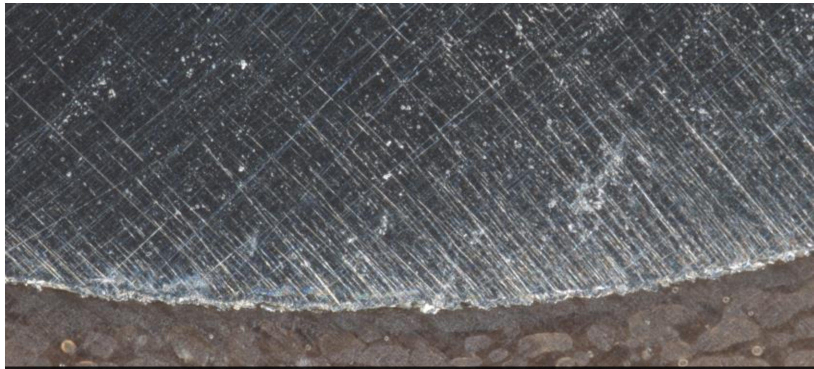

ECTFE – 1mm


ETFE – 1 mm

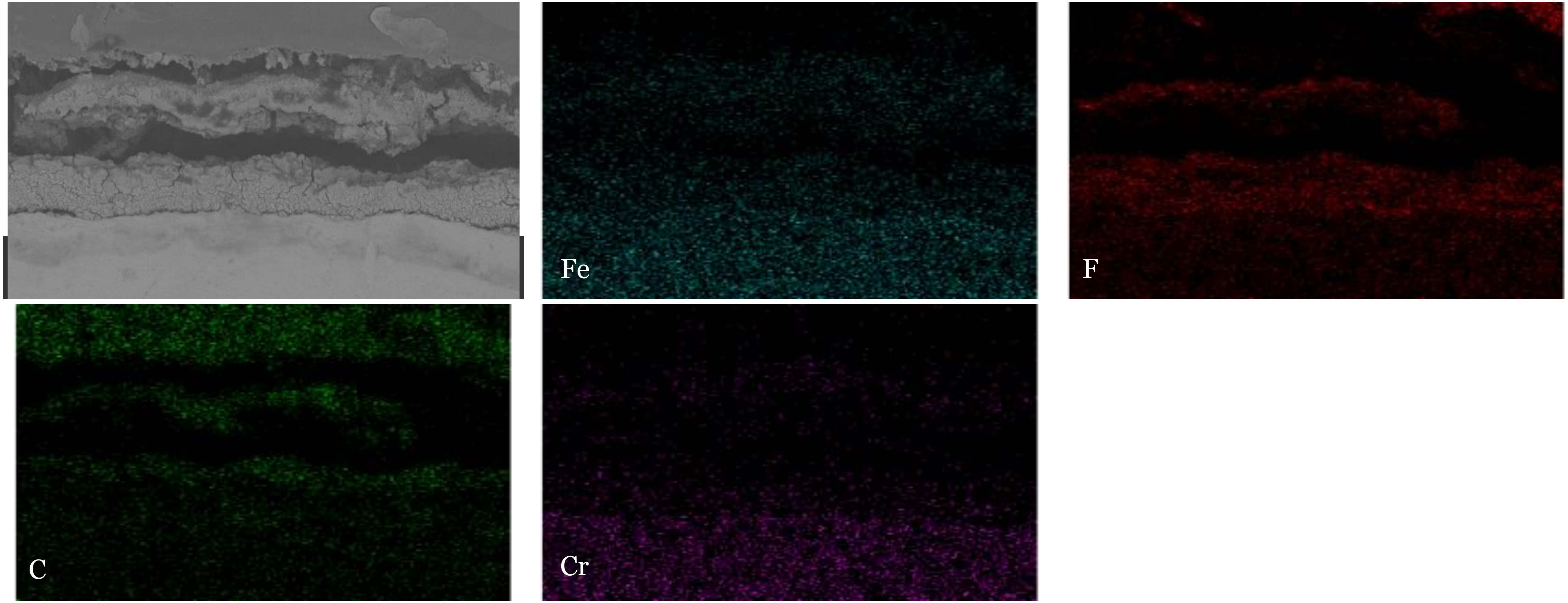

PFA – 1 mm


ECTFE – 2 mm


ETFE – 2 mm


PFA – 2 mm

SEM/EDS of PFA delamination



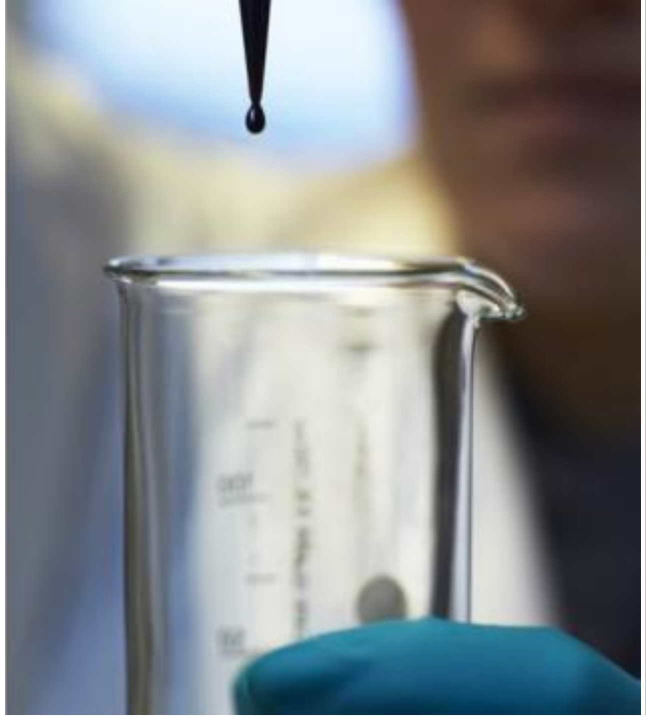
Summary

- In order to improve the life time of the sensors, the failure mechanisms need to be identified. Does delamination have to be limiting? Location of the delamination should have a large impact.
- It seems possible that the determining factor is design/quality of manufacturing rather than coating thickness or choice of fluoroplastics.
- Focus should be on optimizing the coating process including quality controll, using e.g. LASER Shearography.
- Exposure method appears to be working well.
- Seems like LS is a valid NDT to inspect polymer coated samples, and is able of detecting delaminations otherwise only visable by microscopy.

RI. SE

THANK YOU!

QUESTIONS?



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