“Optimisation of the mixed-acid online monitoring and control in stainless steel pickling plants”

BFI Workshop “Pickling Solutions Technology”,
Düsseldorf, 13th November 2019

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Content of Presentation

- Model based online concentration measurement –

  General overview of functionality and developments for HCl-Fe, H_2SO_4-Fe pickling acid systems

- Online concentration monitoring and control at stainless steel strip pickling lines –

  Overview of developments in RFCS Pilot project for HNO_3-HF-mixed acid systems

- Outlook

Online-measuring technique for automated concentration supervision in acidic process bath

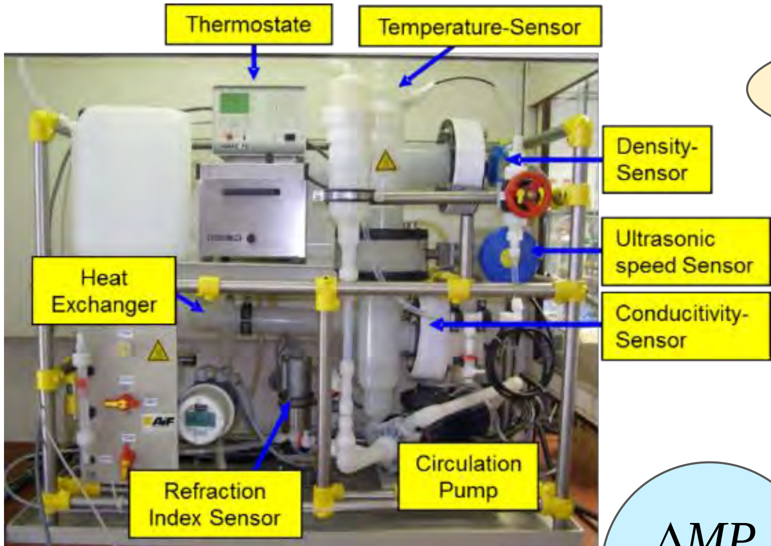
Initial Situation

- Pickling by acid solutions is an important process step for fabrication of highly pure metal surfaces
- Pickling bath supervision by manual process analysis → time and cost intensive
- Not available online-concentration data → automated process control difficult
- High product quality/plant-productivity demands fast adjustment and perpetuation of optimal set points of free acid and metal salts concentrations

Solution

- Development of an operational online-measuring technique for continuous and simultaneous acid concentration analysis
- Application of a model based analysis technique by physical parameter online measurement

Model-based online-concentration analysis for pickling acid solutions (DynAcid®) - Functionality



integral measuring method

operational online-measurement

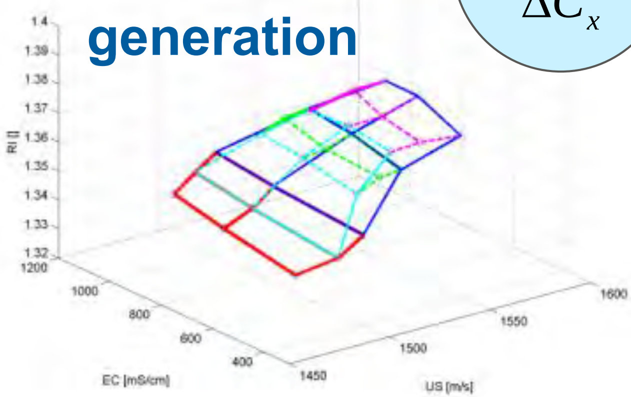
Physical parameter measurements (T, v_{US}, λ_{el} *optional RI or* ρ) continuously in acid solution

Mathematic-physical concentration calculation model

Pickling bath concentrations (2 or 3) continuously + simultaneously

$$\frac{\Delta MP_x}{\Delta C_x}$$

model database generation

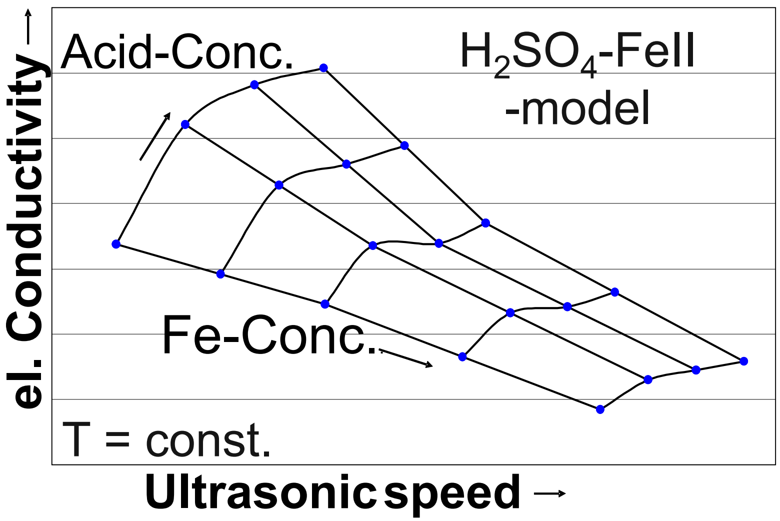


Development of concentration calculation models

Fundamental development of DynAcid®-Technique for HCl- and H_2SO_4-Fe pickling lines

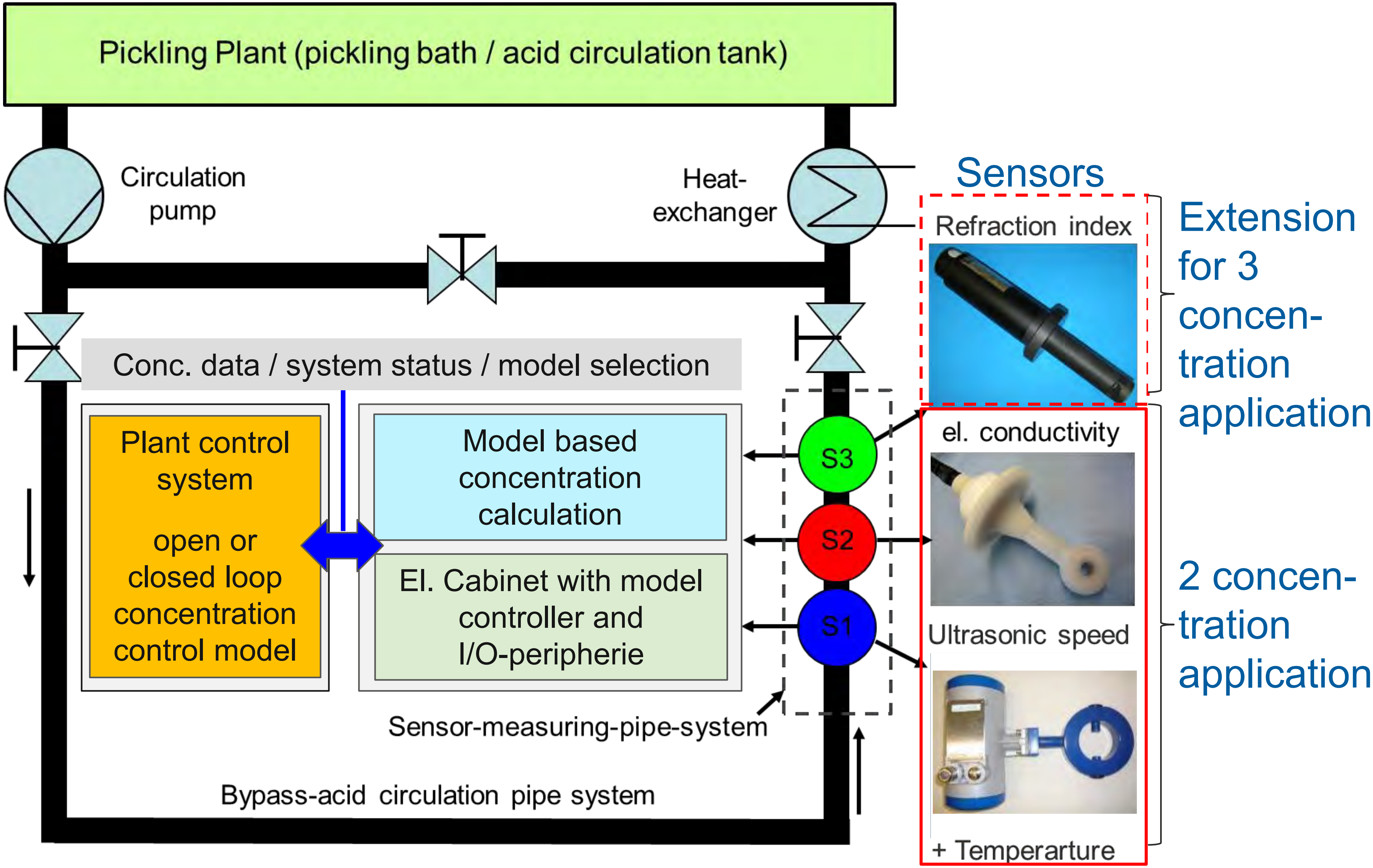
- Basic measuring method developments (model database + cal. model)
- Set-up of measuring technique, testing in laboratory + technical centre

Set of characteristic curves from laboratory investigations



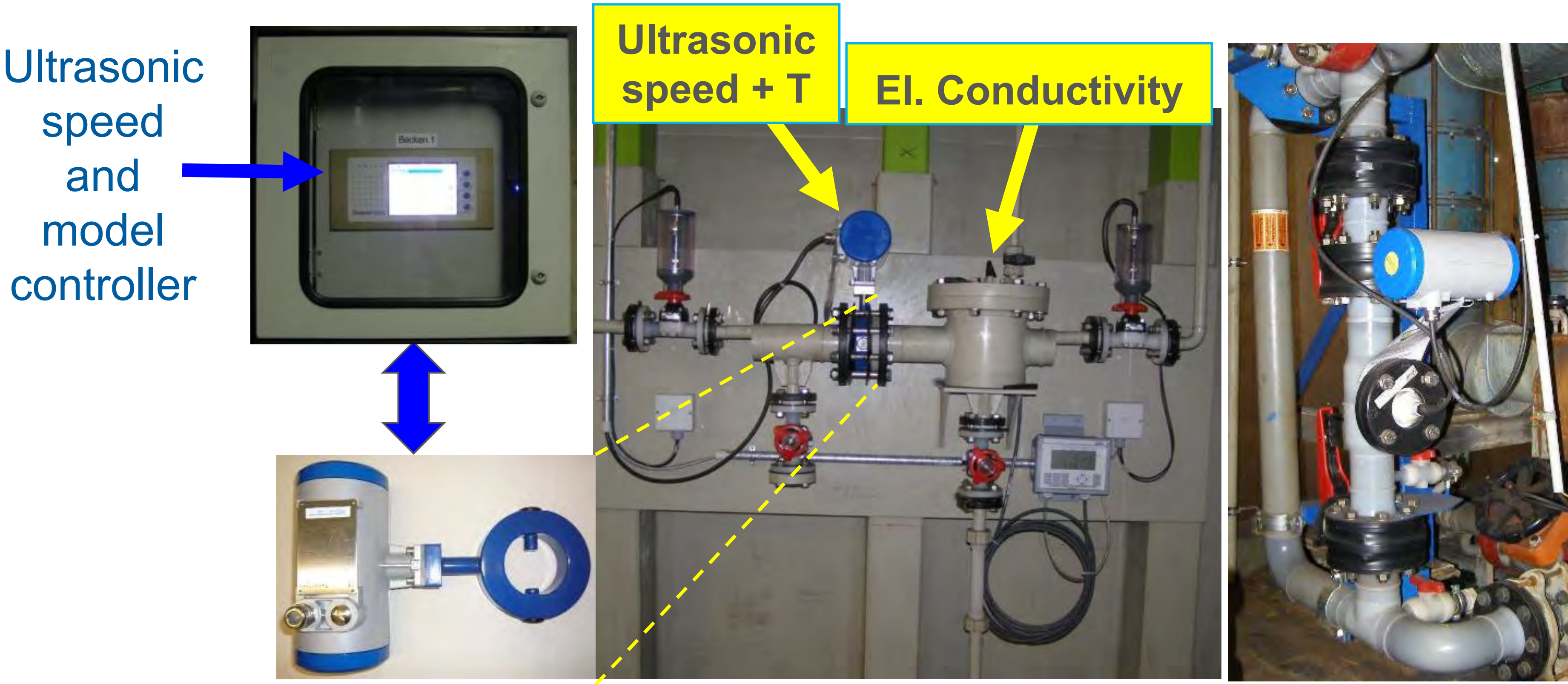
Mobile measuring system
test and demonstration equipment

Concept for operational online measuring system integration at pickling plants



Operational installation of DynAcid®-Technique for HCl- and H_2SO_4-Fe pickling lines

- Examples of operational installations and commissioning

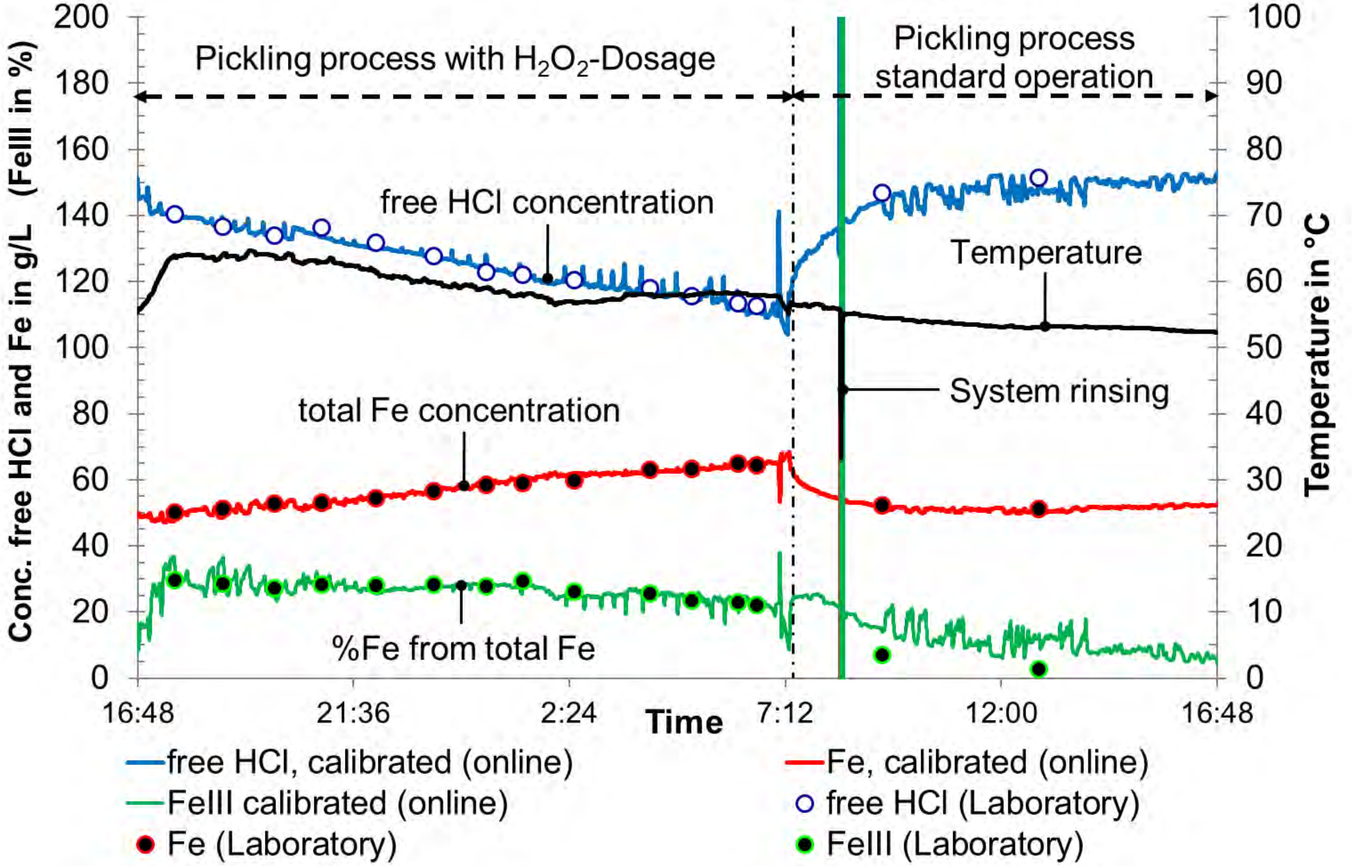


Measuring technique application at pickling lines

Special development of online measuring technique for HCl-FeII-FeIII stainless steel pickling bath applications

› Continuous concentration monitoring and FeIII-FeII-ratio adjustment by H_2O_2-dosage

› Operational demonstration at dip-tank HCl-wire rod pickling plant



Online measuring technique commissioning and operation

- Calibration of model based online analysis systems on operational measuring conditions by laboratory reference analysis
  - differences between artificial model solutions and pickling acids
  - differences in measuring system set-ups
  - specific operational temperature and concentration ranges
- Measuring conditions of acid media: As possible low gas bubble and sludge accumulation, flow rate > ~ 6 m³/h, dT_{sample} < 10 k/h,
- Measurement accuracy: Deviations to reference analysis mainly ~ < 5 g/L Fe and < 8 g/L HCl /H_2SO_4
- Maintenance – depending on operational application:
  - Sensor-(pipe section) rinsing from solid matter (~ every 2 to 7 days)
  - Validation of basic functionalities (~ 2 to 4 times/year)

Commercial availability of DynAcid® online measuring technique for H_2SO_4- and HCl-pickling bath applications

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Sales and distribution + commissioning and support

- BFI Betriebstechnik GmbH (Düsseldorf)
- SensoTech GmbH (Magdeburg-Barleben)
  + Ultrasonic speed sensor and model controller technique

Specially offered measuring technique service options by BFI

- Consulting concerning system installation and operation
- System commissioning on-site the operation locations
- System calibration on operation conditions by reference analysis
- System maintenance (online sensor dismounting, cleaning and validation, failure analysis and repair support)
- System demonstration installations

Overview DynAcid®-Installations by BFI + BFI-Betriebstechnik GmbH (inclusive commissioning)

- HCl-pickling lines (each 2 systems)
  - DEW (Germany, dip-tank wire rod pickling), ~ 2006 →
  - TKSE (Germany, strip pickling line), ~ 2007 →
  - Turkey (Iskenderun, strip pickling line), ~ 2011 →
  - South Korea (Pohang, strip pickling line), ~ 2012 →
- H_2SO_4-pickling lines
  - TKS (Germany, strip pickling line) → 4 systems, ~ 2008 →
  - TK (Germany, strip pickling line) → 2 systems, ~ 2009 → ~ 2015 (facility closed)

MACO-Pilot – Optimisation of the mixed-acid online monitoring and control in stainless steel pickling plants

RFCS Project (07/2016 – 12/2019)

› Optimisation of the online concentration measuring technique for different HF-HNO_3-mixed acid pickling plant applications

- calculation model enhancement, system set-up, sensor-lifetime

› Operational installations and optimisation of prototype systems at stainless steel strip and wire rod pickling plants

› Improvement of the pickling process operation at stainless steel pickling plants

- Closed loop control model, pickling programme management tool

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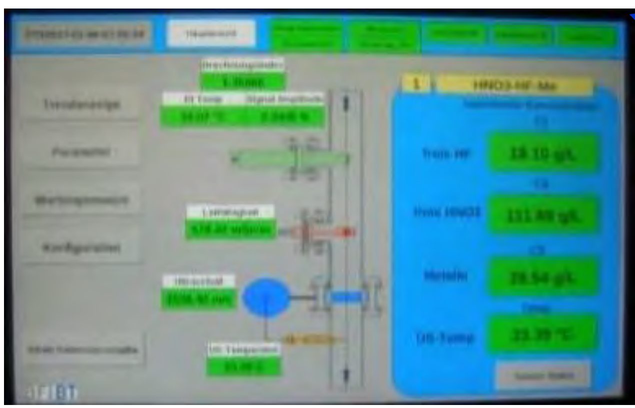
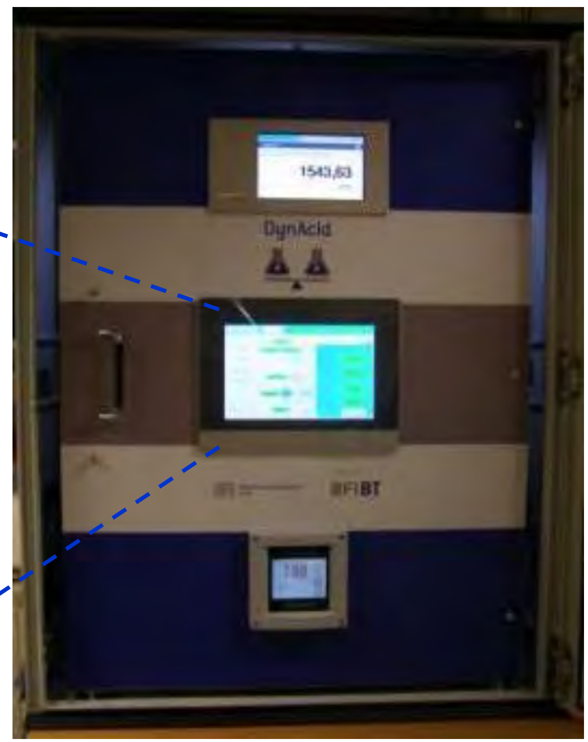
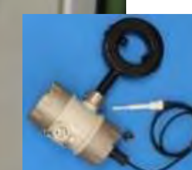
Optimisation of online measuring system set-up for HNO_3-HF mixed acid applications

- New types of sensors for refraction index and ultrasonic speed measuring
- New el. cabinet model-controller and physical parameter sensor-measuring pipe set-up

Main Data Screen

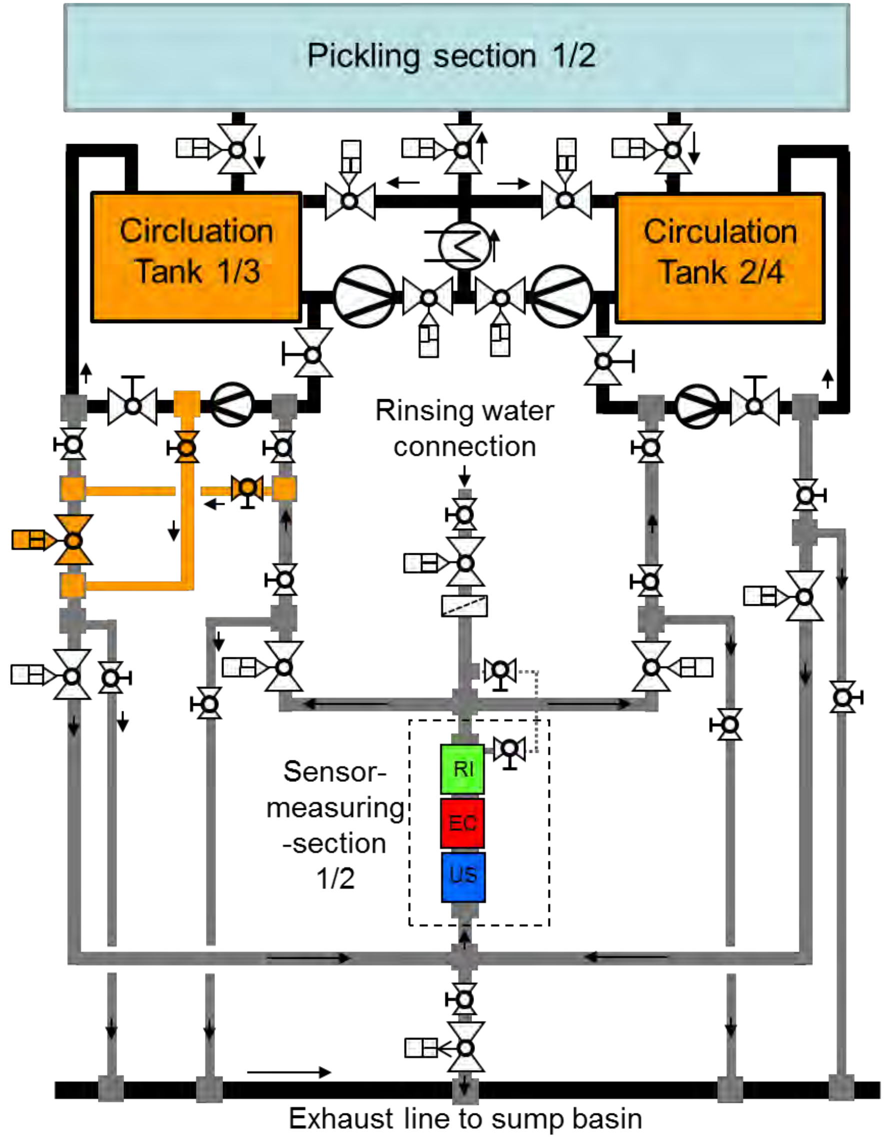






Integration of online concentration measuring prototype systems – example for a modern strip pickling line

- 2 acidic pickling sections with 2 acid circulation and storage tanks per section
- Fast pickling programme change by switching between 2 different bath concentrations (e.g. ferritic / martensitic)
- Installation of 1 online measuring system per section
- Supervision of acid circulation tanks by automatically controlled switching
- Automatically controlled sensor measuring pipe water rinsing



Example for realised online concentration measuring prototype system installation at strip pickling line

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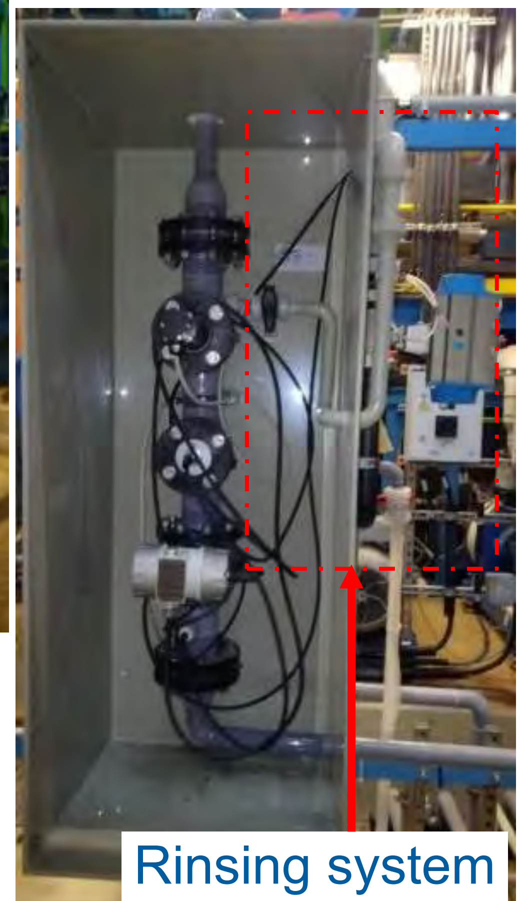
Integration of an online measuring systems at strip pickling line

Sensor measuring pipe system



Connection to acid circulation system

Example of advanced closed-loop concentration control model for strip pickling lines

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- Temporary (~ 4 – 8 h) - atline-analysis data for acid circulation + regenerated acid tanks

- Online-analysis system status information and operation mode
- Online analysis data of the acid circulation and regenerated acid tanks

Additional process + plant data: e.g.
- Pickling plant operation mode
- Active circulation tanks
- System volumes, tank level set points
- Concentrations of fresh acids
- Regenerated acid supply status
- Set points for tank acid concentrations
- Dosed volumes of acids and water

Tank No.

o.k.?

Advanced concentration control model

open loop

manually / automatically

closed loop

- Calculated tank dosing volumes for acids and H_2O
- Calculated tank acid concentrations and tank levels
- SPC Control signals (e.g. dosage valves, pumps)
- …

Concentration monitoring and control at strip pickling line by manually operated pickling bath concentration control

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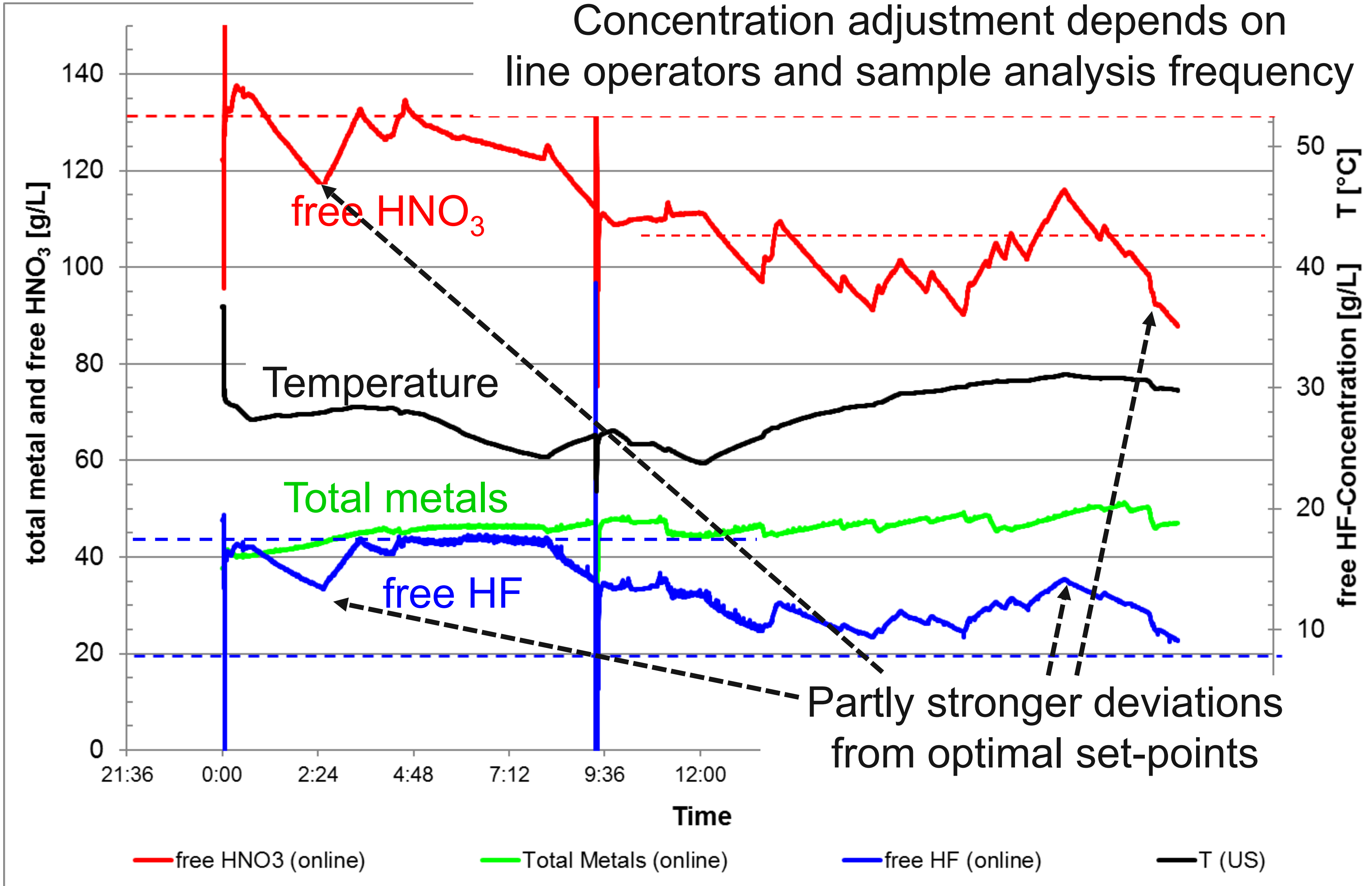
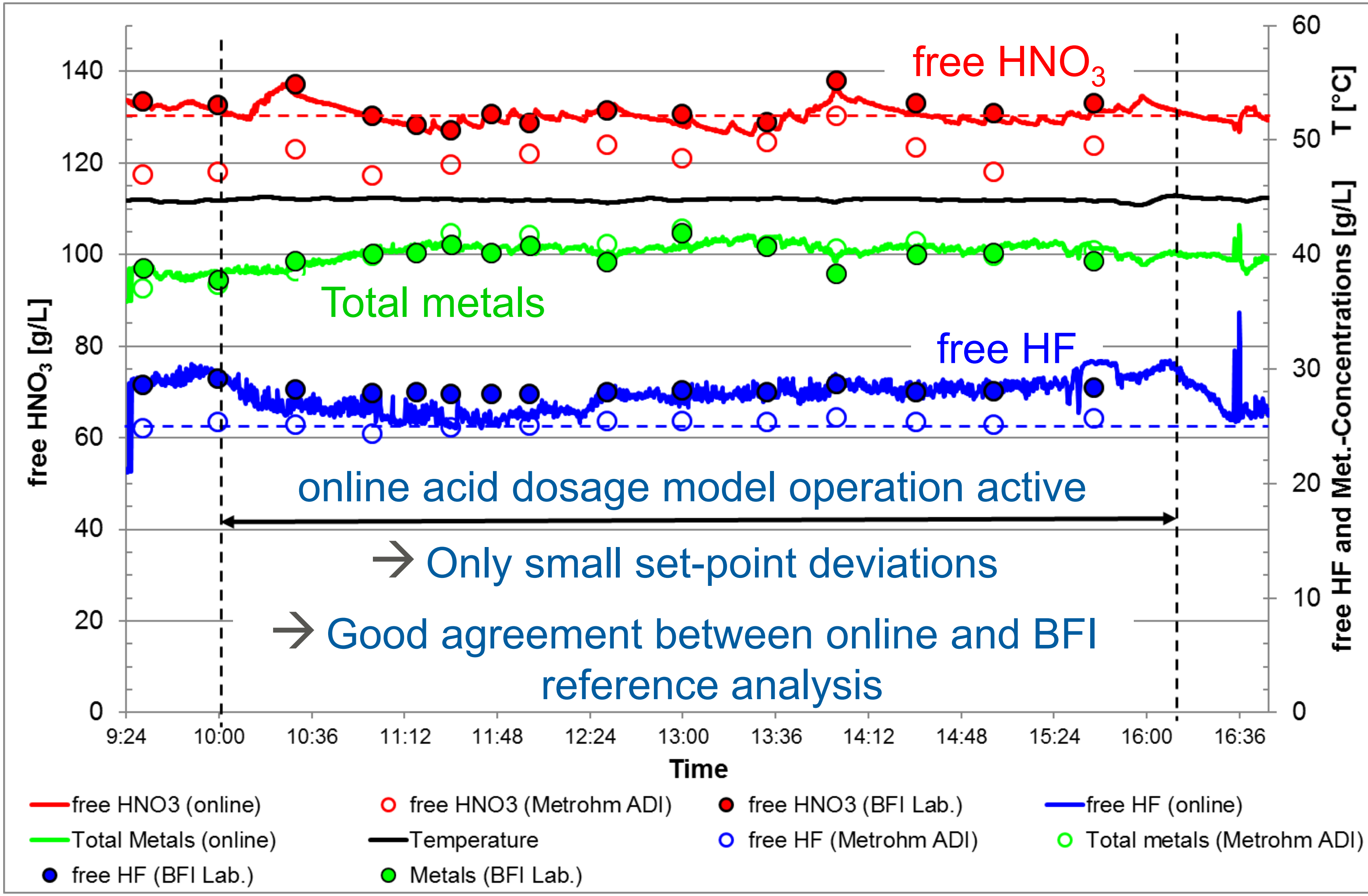


Concentration monitoring and control at strip pickling line by automatic online pickling bath concentration control



Summary of current MACO Pilot results

- Optimised online-measuring system prototype set-up
- Successful installations of online measuring systems at strip and wire rod pickling plants
- First testing of closed-loop online concentration control model for strip pickling process shows good results
- Online measuring system functionality and analyses accuracy depends on operation conditions (e.g. gas bubble and sludge accumulation)
- At present, deviations between online analysis and BFI laboratory reference analysis mainly < ~ 5 g/L for free HF + total metals and < ~10 g/L for free HNO_3 concentration
- Enhanced information concerning online sensors operational life-time experiences (at present ~ 2 - 6 years)

Outlook

RFCS Project MACO Pilot

- Further optimisation works and tests at the pickling plant applications → 12/2019
- Further optimisation of concentration calculation models → 12/2019
- Realisation of marketable measuring technique on basis of the experiences and prototype system set-up, 1/2020 →

Ongoing online measuring system application developments

- H_2SO_4-Zn-Fe acid solution mixtures (recovery of Zinc from steel scrap)
- HNO_3-H_2SO_4-Zn acid mixtures (surface treatment of Zn products)
- …

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“Operational experiences of process bath analysis in a wire rod pickling plant”

BFI Workshop “Pickling Solutions Technology”,
Düsseldorf, 13th November 2019

Frederik Kolinke
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VDEh-Betriebsforschungsinstitut GmbH

Stahl

Content of Presentation

- Overview of DEW wire rod pickling plants for carbon steel and stainless steel
- Online concentration monitoring at HCl-Fe wire rod dip tank pickling plant
- Online concentration monitoring at HF-HNO3 mixed acid wire rod dip tank pickling plant (project MACO Pilot)
- Summary and outlook

Wire rod production at DEW Hagen

Wire rod production at DEW Hagen

Production Site Hagen:

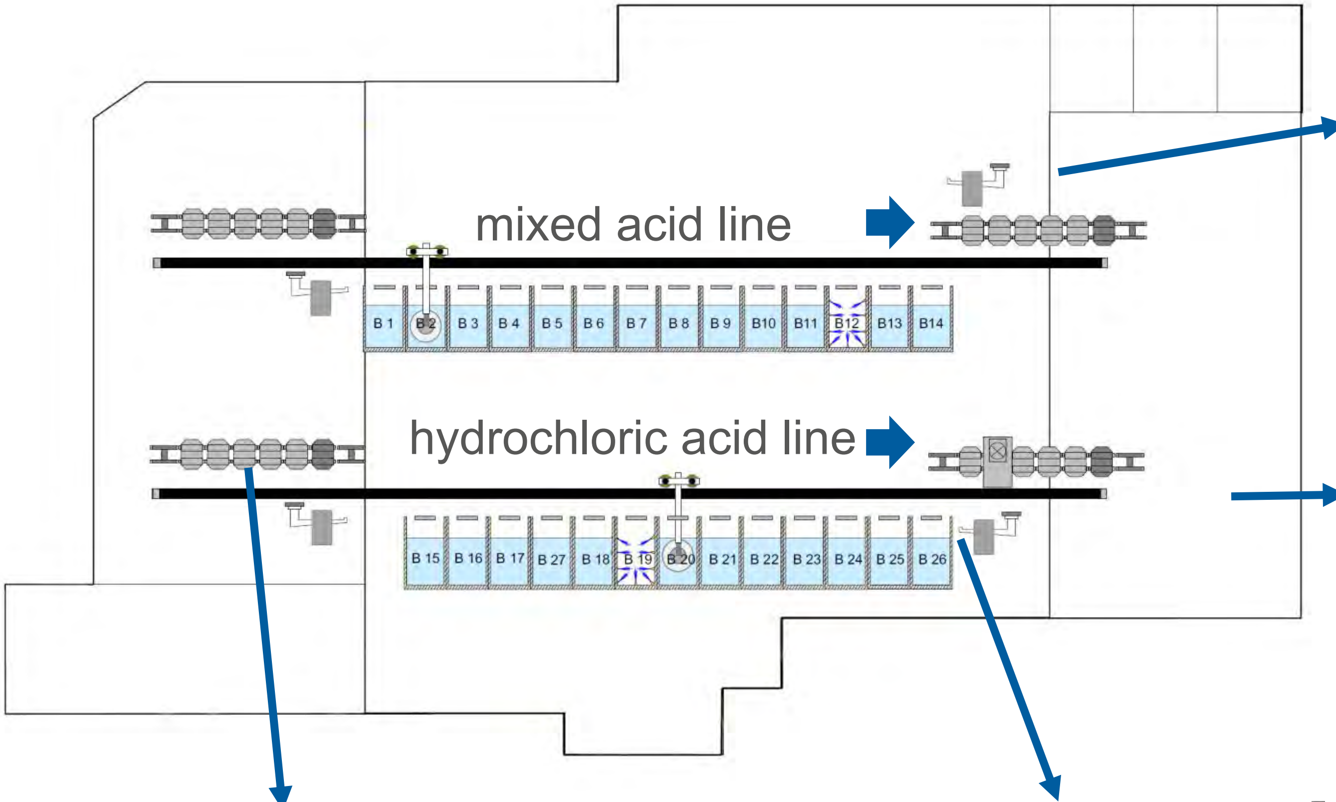
- 400 Employees
- Output per year around 100.000 t
  - ca. 59 % Construction Steel
  - ca. 37 % Heat and Acid Resistent Steel
  - ca.   4 % Tool Steel

Main products:

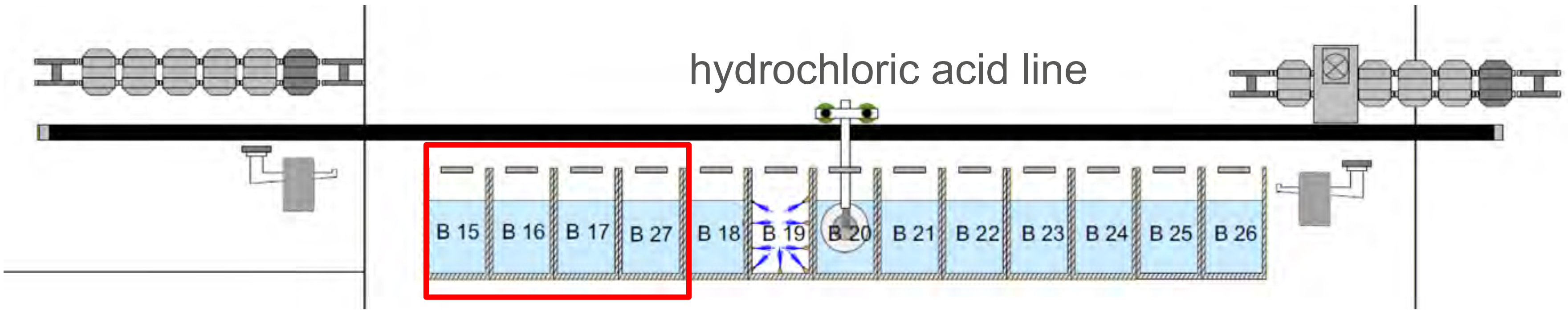
- Wire rod steel : Ø 5,5 bis 30 mm
- Bright Steel
  - Long Products : Ø 2 bis 26 mm, length from 250 bis 6200 mm
  - Wire rod: Ø 4 bis 22 mm

F. Kolinke, (DEW)· M. Werner, M. Kozariszczuk ·

Wire rod pickling plants



Online-measuring technique for automated concentration supervision at wired rod HCl-pickling plant



Operation HCL Pickling

- Pickling of Construction Steel, Bearing Steel
- 4 HCL pickling baths, management of
  - HCL concentration in g/l
  - Fe concentration in g/l
- Both values need to be maintained inside certain tolerances

Online-measuring technique for automated concentration supervision at wired rod HCl-pickling plant

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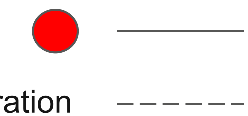
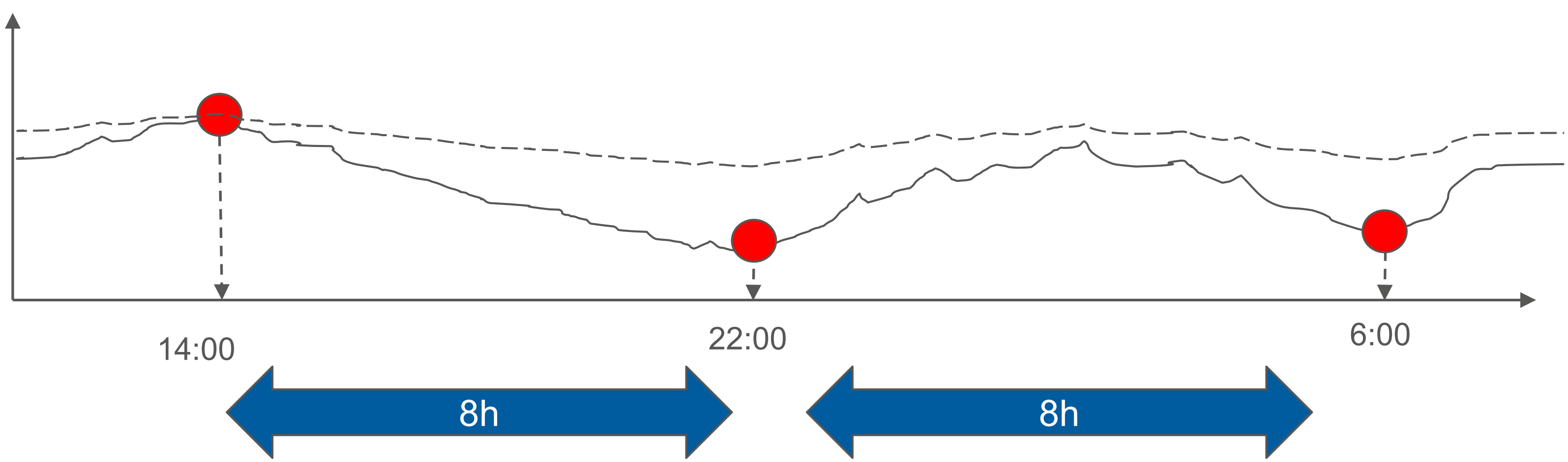
Online- Measuring – Advantages

- Offline – measurement – samples every 8h
- Concentration management auto dosing depending on Amount of pickled material
- With offline concentration measurement:
  - Uncertainty in acid and iron concentration between samples for 8h
- With online concentration measurement:
  - Increase in accuracy maintaining a certain value of acid and iron concentration





Online-measuring technique for automated concentration supervision at wired rod HCl-pickling plant

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Operation of Online- Measuring

- Two sensors per measurement unit
  - Ultrasonic and conductivity sensor
- 2 Units for 4 HCL Pickling Baths
- Positioned inside the heating Loop
- Continous Measurement and Visualization of
  - HCL Concentration in g/l
  - Fe Concentration in g/l

Maintenance of Online - Measuring

- Rinsing with NaOH once per month for 24h
- Every 6 month visual inspection and recalibration
- Operation since 2006 (13 years)

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Concentration monitoring and control at stainless steel wire rod mixed acid pickling (Project MACO Pilot)

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Operation Mixed Acid Pickling

- Pickling of Heat and Acid Resistent Steel
- 5 mixed acid pickling baths, management of
  - HF concentration in g/l
  - HNO3 concentration in g/l
  - Fe concentration in g/l
- All three values need to be maintained inside certain tolerances

Concentration monitoring and control at stainless steel wire rod mixed acid pickling (Project MACO Pilot)

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Initial situation at mixed acid line

- The bath concentration supervision by at-line analysis is time consuming (manual sample drawing, analysis time about 30 minutes per tank sample) and thus the sample frequency limited to about 8 h.
- Some steel grades can cause high temperate increase >> 40 °C in the pickling tanks during the complex chemical reactions of the HF-HNO3-acid mixture
- The adjustment of the acid concentration within the set-point ranges and the control of the tank temperature is very import for save process control

Solution

- Additional installation of an high-rate mixed acid analysis system

Concentration monitoring and control at stainless steel wire rod mixed acid pickling (Project MACO Pilot)

Special Conditions inside miced acid line

- Problem: Very high solid matter accumulation in pickling acid >> 10 g/L

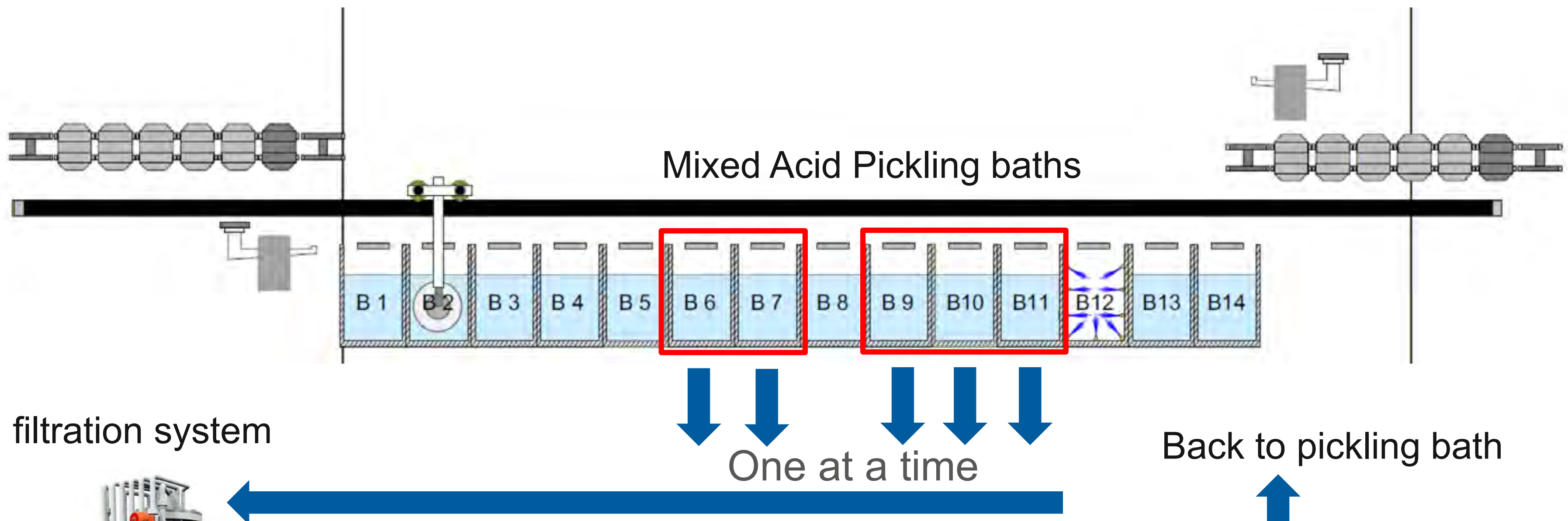
Solid matter inside
Pickling bath

- Refraction index sensor functionality of online analysis system limited to 9 g/L

Solution

- Solution: online analyser sample stream pre-treatment by filtration system

Concentration monitoring and control at stainless steel wire rod mixed acid pickling (Project MACO Pilot)



Source: Scanacon

BFI Online Analyser

- One Unit for 5 pickling baths
  - Refraction index sensor
  - Ultrasonic sensor
  - Conductivity Sensor
  - Temperature Sensor
- Start of Operation Beginning of 2018

Integration of concentration measuring system / filtration technique at the DEW mixed acid wire rod pickling plant

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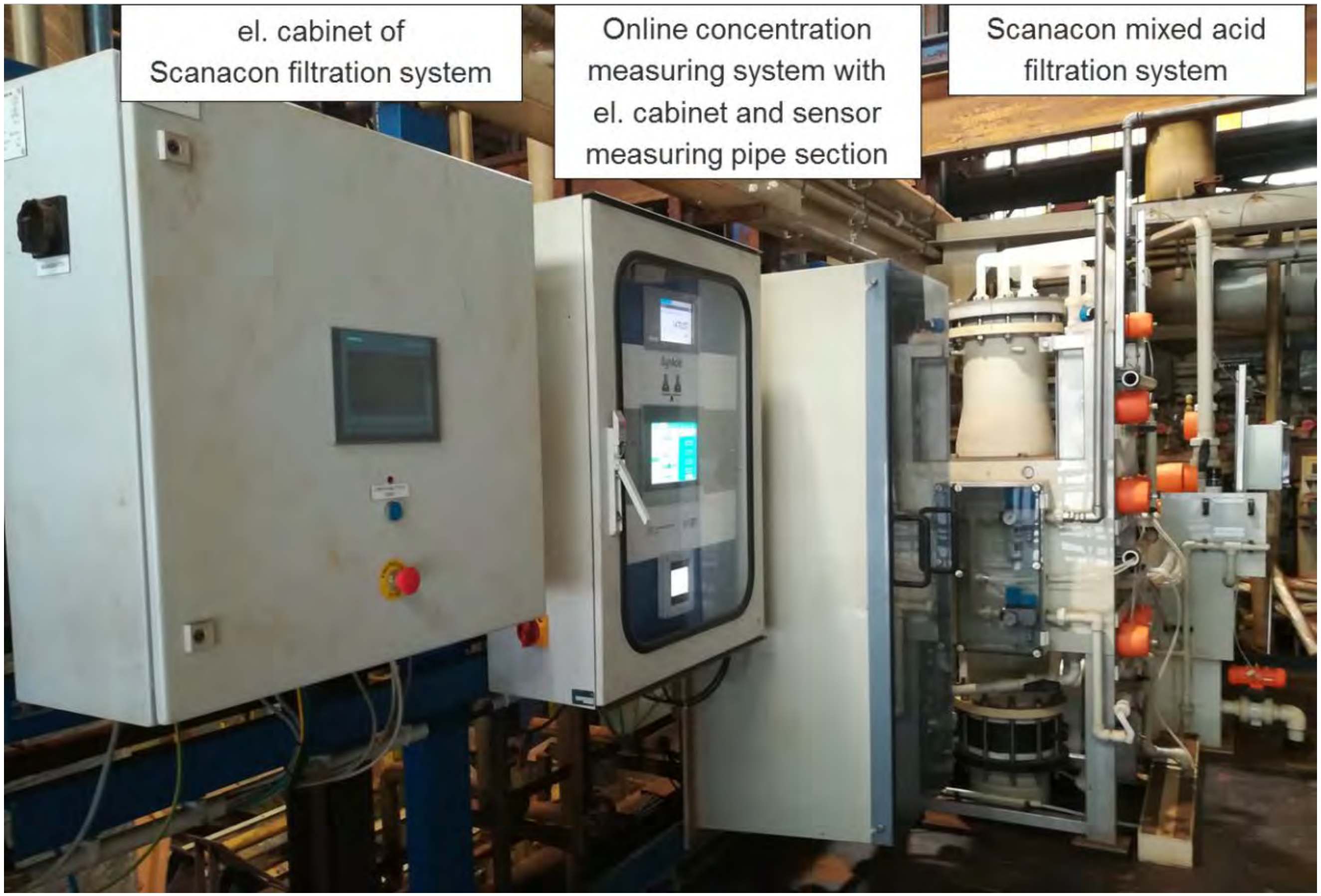
› Installation of the equipment



Summary of current main project results

- Successful installation and commissioning of filtration technique and online concentration measuring system
- The pickling tank concentration monitoring frequency can be increased from about 8 h (by chemical at-line analysis) to about 2,5 h by application of the online analysis.
- The combination of at-line analysis and online-analysis enables a significant improvement of the pickling process control (faster adjustment of bath concentrations by open-loop correction dosage of acids + reduction of critical process conditions / better management of autocatalytical process conditions)
- Online analysis system functionality and analyses accuracy depends on operation conditions (e.g. higher gas bubble accumulation in sample stream after filtration technique, low flow rates, temperature oscillations > 10 k/h during pickling tank switching …)
- At present, after calibration deviations between online analysis and BFI laboratory reference analysis < +/- 5 g/L for free HF and total metals and < 10 g/L for free HNO_3 concentration (under ideal measuring conditions)

Workshop on Pickling Solutions Technology

Optimisation of pickling process control and management by model-based simulation tools

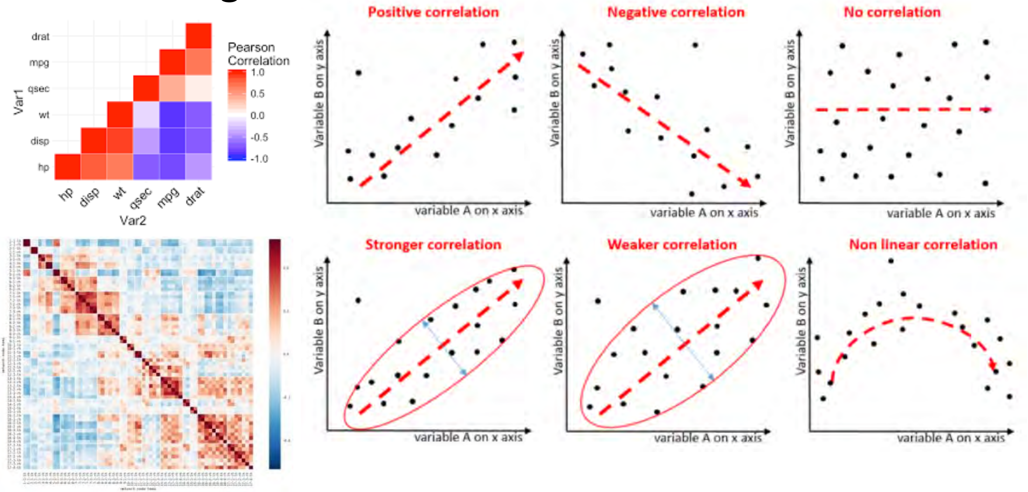
University of Oviedo
Iván Machón González

13th of November 2019, Düsseldorf

Optimisation of pickling process control and management by model-based simulation tools

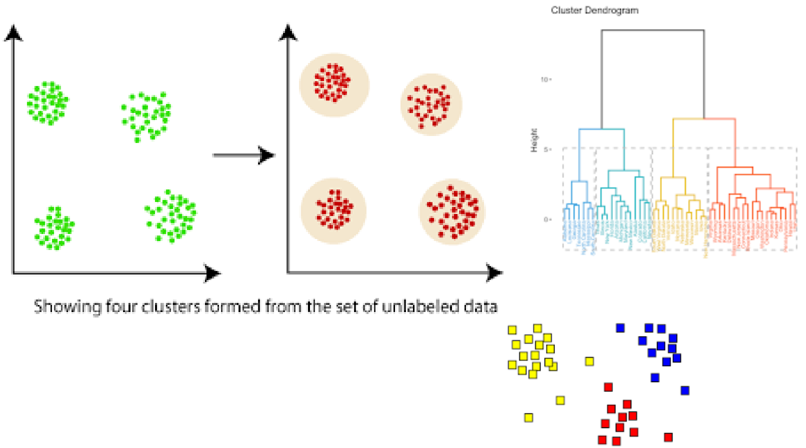
Data correlations

- Analysis and/or verification of correlations
- Search of nonlinear or partial/local correlations by means of visualization algorithms



Data clustering

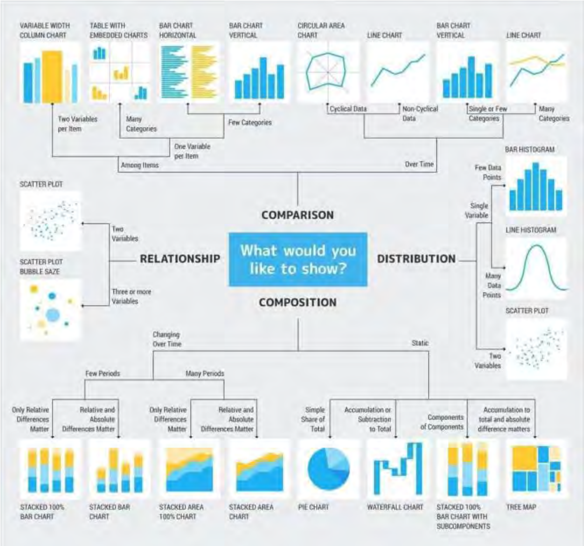
- Some algorithms can be used for cluster analysis. Search of common patterns by means of merging similar samples.
- Classification tasks.



Optimisation of pickling process control and management by model-based simulation tools

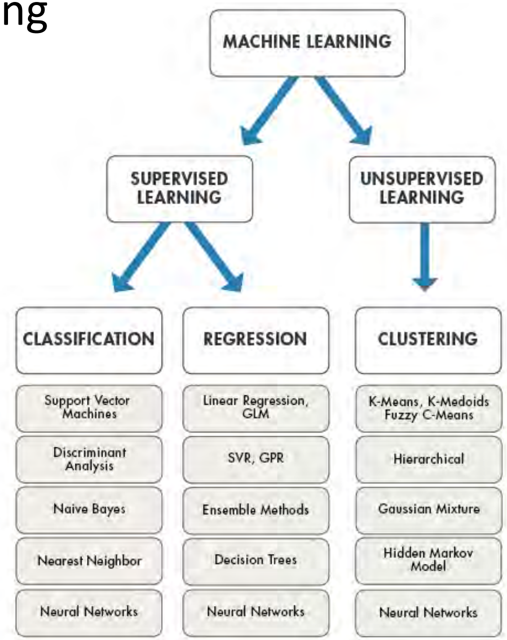
Data representation

- Data representation (e.g. plots, barcharts, etc.) of results for further discussion with experienced personnel.



Machine Learning algorithms

- Supervised versus unsupervised learning

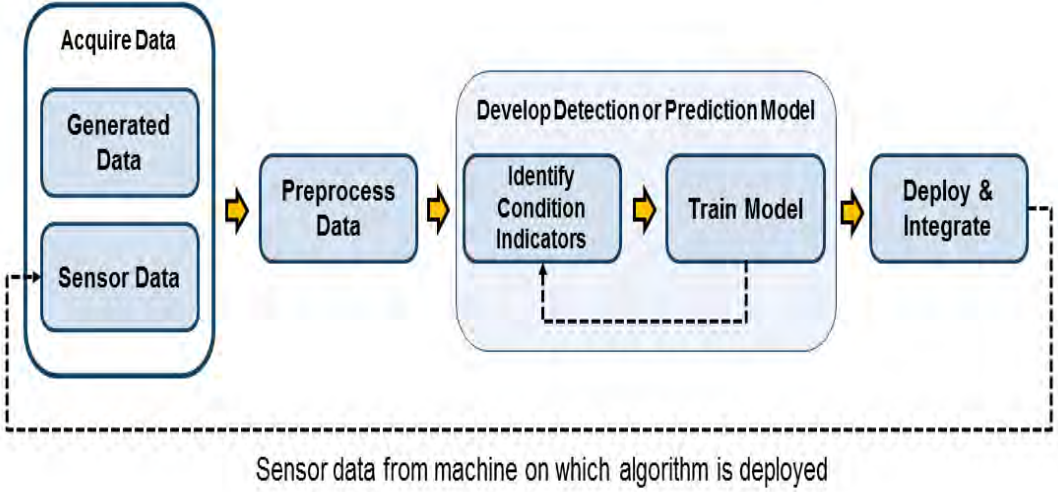


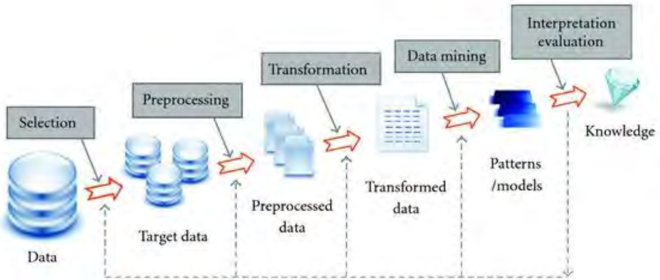
Optimisation of pickling process control and management by model-based simulation tools

Development of the process model

- Condition Monitoring and Predictive Maintenance

General procedure





SensorControlPilot (I)

- Estimation the pickling strip speed by means of a model that indicates the mean values and standard deviation of the maximum speed for different conditions in the pickling line.

- Neural Gas network as model to establish a probabilistic distribution of the pickling line speed. The main idea is to calculate the optimum strip speed of the pickling line given the remaining process variables. Data from the hot rolling mill and the pickling line were used.

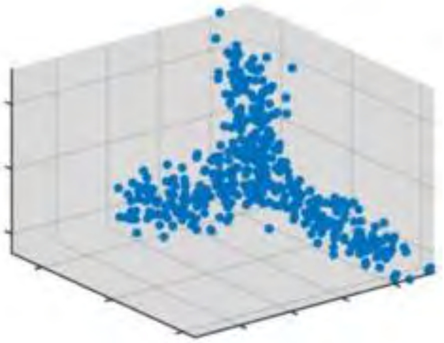
- Two different trained models were considered depending on the material destination: chromium or tin.

- The aim is to obtain a set of prototypes of coils by the application of this kind of algorithms. These prototypes are synthesizing all the information of the coils and they can be used to estimate the optimum strip speed of the pickling line.

SensorControlPilot (II)

- The following process variables were used to train the neural model:
  - for tinned material destination: hot rolling coiling temperature, initial strip temperature, iron concentration in bath 1, acid concentration in bath 1, steel type, destination, strip thickness, strip width and pickling line speed.
  - for chromed material destination: hot rolling coiling temperature, destination, steel type, iron concentration in bath 1, acid concentration in bath 1, pickling line speed and strip thickness.

- The euclidean distance within input data space
  for taking out the estimation of the strip speed setpoint.



MACOPilot

Development of an innovative pickling program management model based on online data of the wire rod pickling plant process.

- Specification of the pickling dwell time before the beginning of the pickling treatment by the management software tool.

- Selection of the dip tank by means of the management model based on the current process data for optimal pickling result.

- Simulated testing of the new pickling program management for wire rod pickling plant operation of DEW

Initial study of the variables affecting the effectiveness of the pickling process

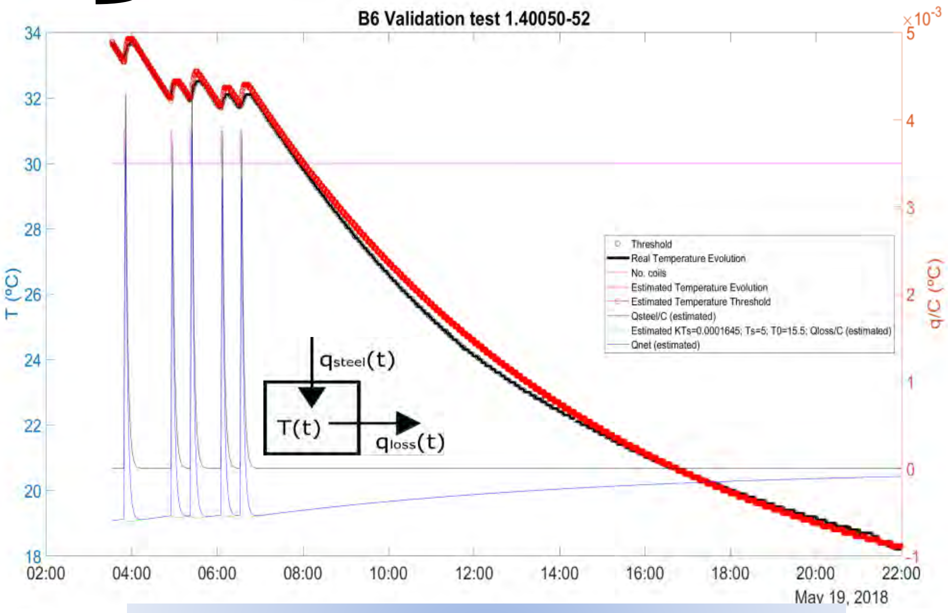
- Acid mixture composition and free Fe content. → stable due to acid bath regenerations.
- Steel type and allow composition.
- Previous heat treatment (austenization, annealing, tempering…).
- Dwell time and number of consecutive pickling operations.
- Hydraulic conditions in the acid baths.
- **<u>Mixed acid bath temperature.</u>**

Fixed variables in the process datasets (dictated by steel code)

The temperature dynamics in the pickling baths are increased during the treatment due to the combination of the pickling exothermic reaction and the cooling system refrigeration.

The **control of the temperature** is essential for the development of the pickling:

- Too low temperatures decrease the efficiency of the pickling reaction (poor treatment results): recommended to pickle over 25 ºC.
- Too high temperatures affect the results of the pickling (more risk of overpickling and toxic steam emissions): higher temperature limit set at 40-45°C.

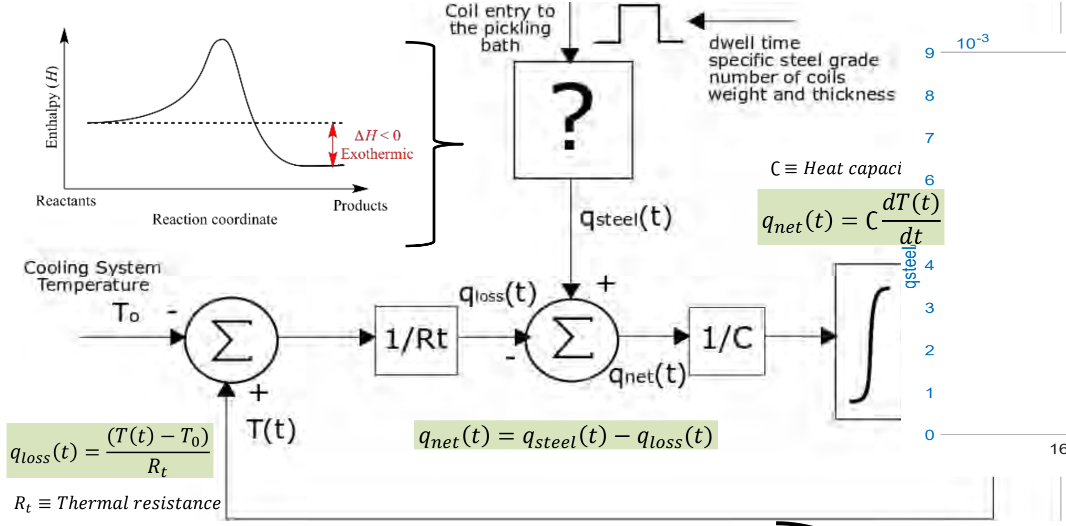


Necessary to develop a model of the temperature dynamics which can predict its evolution. →

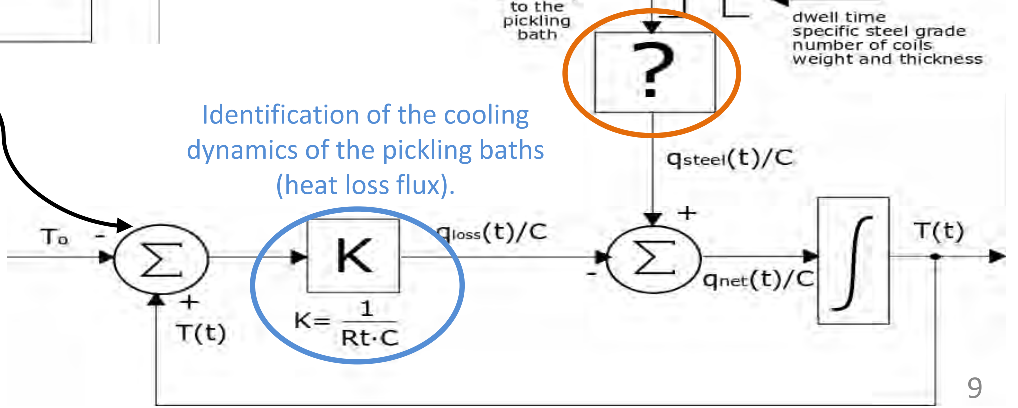
Identification of the heat flux distribution due to:

- Pickling exothermic reaction.
- Cooling system dynamics.

Development of the pickling programme management model



Obtaining the heat flux distribution corresponding to the temperature evolution as a result of the combination of the cooling system and pickling reactions.



Analysis of process variables influencing heat flux and temperature evolution

Important differences between each **type of steel**

- Martensitic: special care (reaction triggered, steam emission, short dwell times).
- Austenitic and duplex: hardest to pickle, not important for temperature troubleshooting or overpickling.
- Ferritic: easiest to pickle, medium size dwell times.

Noticeable differences between steels of each category → The more alloy, the more difficulty in pickling. → TF model for each steel code

↓

The **amount of previous pickling stages** carried out affects the subsequent pickling operation. → **TF model for each steel code in each pickling stage**

Reducing the shooting of the temperature (since a large part of the scale has already been eliminated previously).

Analysis of process variables influencing heat flux and temperature evolution II

Fixed dwell times for each pickling programme
Exothermic reaction not finished before the coil is taken out → Martensitic steels

↓

Speed of chemical reaction affects the heat flux produced by the exothermic reaction of each pickling operation.

Variable equivalent to reaction speed →

$$\gamma = \frac{\left(\frac{Qsteel_{max}}{C}\right)}{Dwell\ time}$$

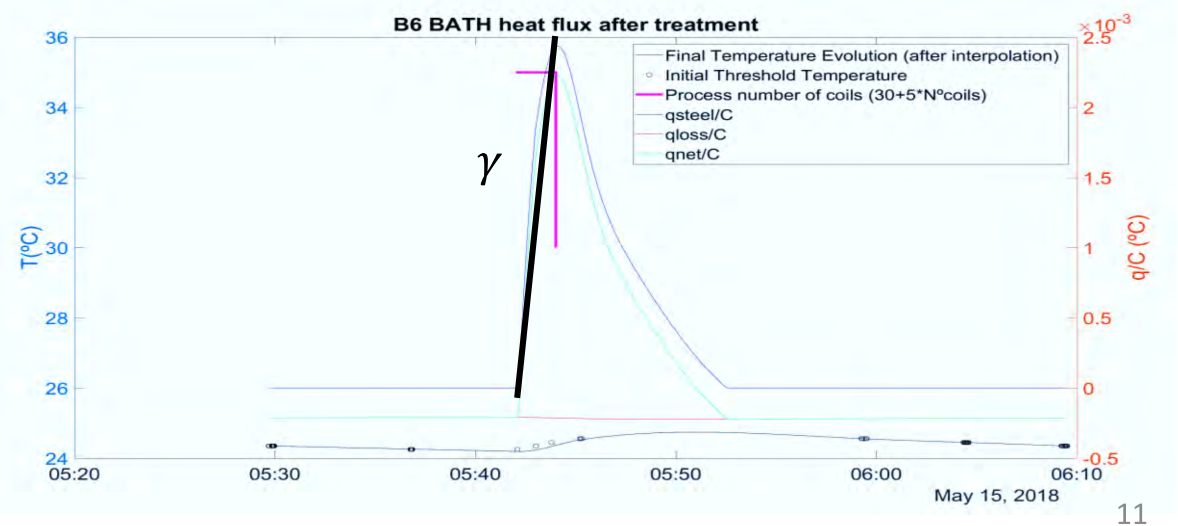
Average speed of the heating

↓

Temperature evolution affected by the speed of the reaction.

$\uparrow \gamma \longrightarrow \uparrow Qsteel_{max} \longrightarrow \uparrow$ Temperature triggering

(for a fixed dwell time)



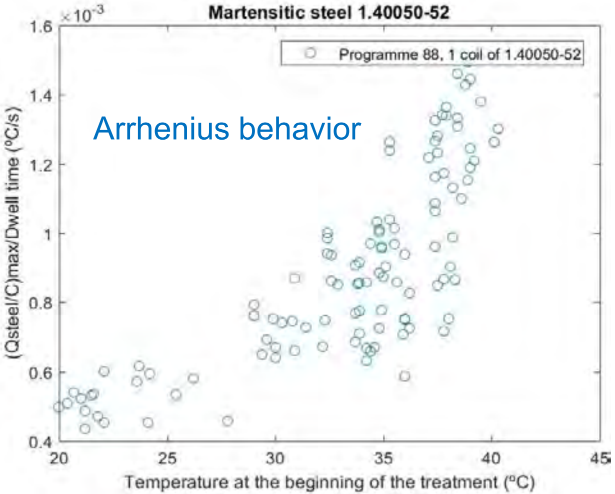
Analysis of process variables influencing heat flux and temperature evolution III

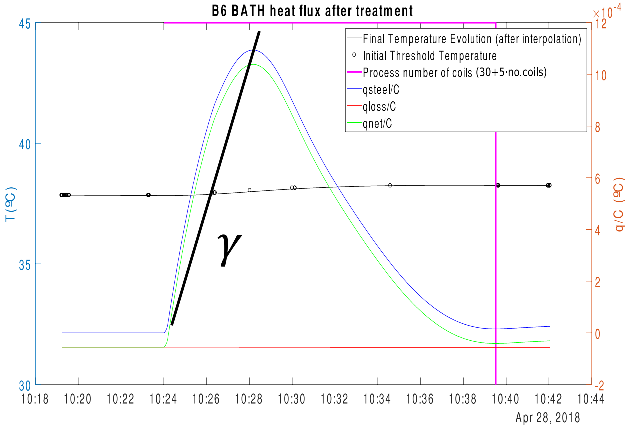
- Variables affecting the speed of the chemical reaction due to the pickling process

Temperature of the bath (ºC)

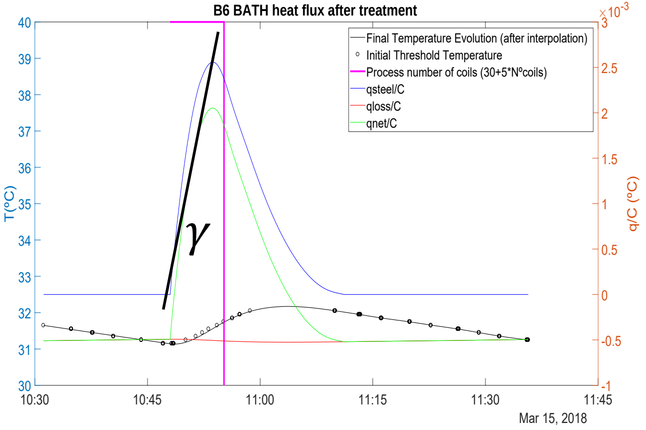
Affects the speed of temperature heating and cooling

- Higher dependence for martensitic steels
  - Lower dwell times (≈ 3 min).
  - Reaction not completed when the coil is taken out of the bath.
  - Greater temperature triggering for higher bath temperature.
- Medium dependence for ferritic steels
  - Medium dwell times (≈ 8 min).
  - Reaction almost completed before the coil is taken out of the bath ($Qsteel_{max}$ reached).
- Lower dependence for austenitic/duplex steels
  - Higher dwell times (≈ 15 min).
  - Reaction and temperature triggering completed before the coil is taken out of the bath.





Heat flux distribution, three coils of duplex steel 1.44620-54 (B6 tank)



Heat flux distribution, two coils of ferritic steel 1.47420-02 (B6 tank, BP 40).

Analysis of process variables influencing heat flux and temperature evolution IV

- Variables affecting the contact surface area for the reaction

Weight (Kg) and thickness (mm) of the coil

- Considering **approximately the same density** for every steel type, they can be considered as the variables to evaluate the influence of the pickled surface in the reaction.

Contact surface $A \approx \pi D L$

Volume $V = \frac{\pi D^2}{4} L$

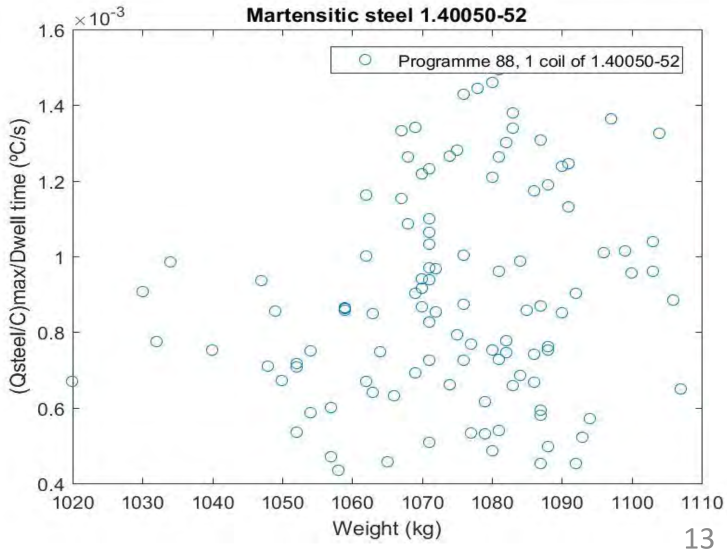
$V \approx \frac{DA}{4}$

For coils of the same weight, $V_1 \approx V_2$

$A \approx k \frac{1}{D}$

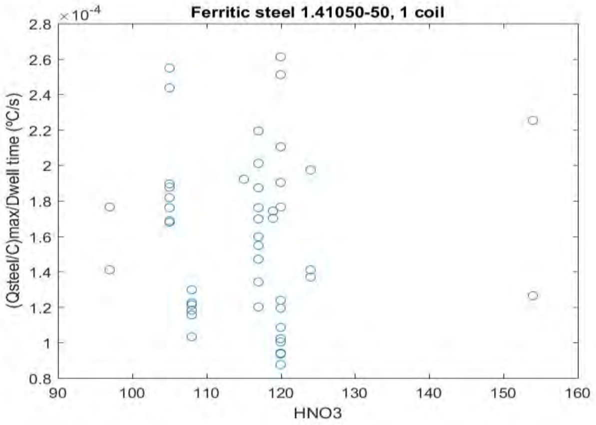
- The higher the weight, the higher the volume and the greater the contact surface.

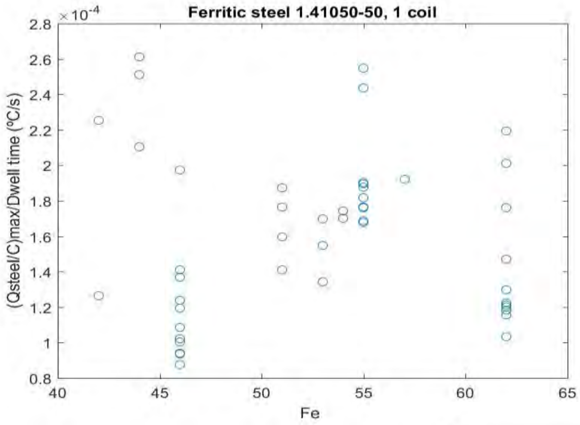
$W \approx V \approx k' A$

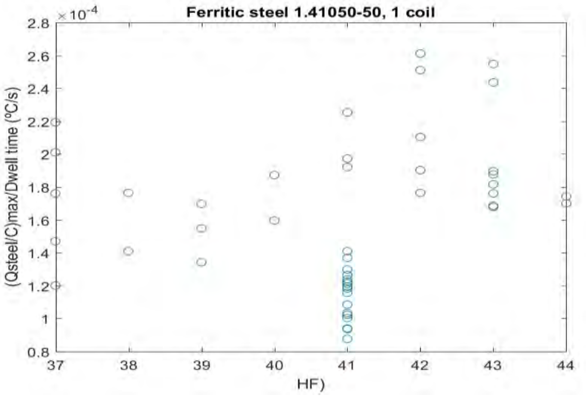


Analysis of process variables influencing heat flux and temperature evolution V

Influence of the % of acid and free Fe in the dynamics of the temperature and heat flux

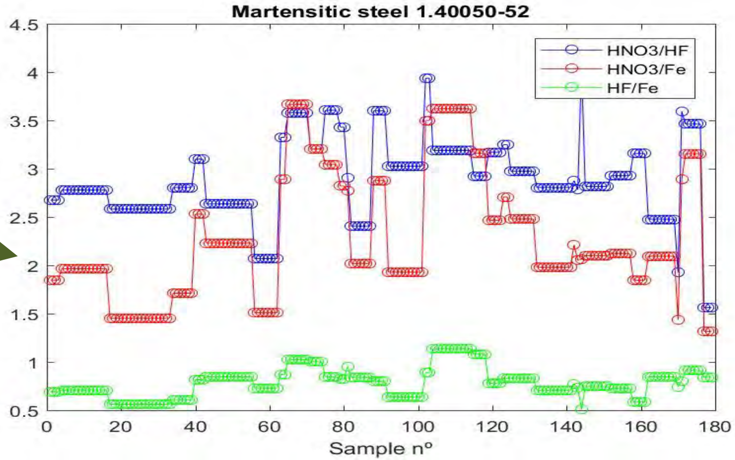






important for the efficiency of pickling process and avoiding overpickling or underpickling (relation free HF/Fe salt)

Relation between free HNO_3, free HF and Fe salt concentrations → Controlled due to pickling bath regenerations (open-loop concentration control system)



Obtaining the pickling TF models (Identification of the heat flux due to the pickling reaction)

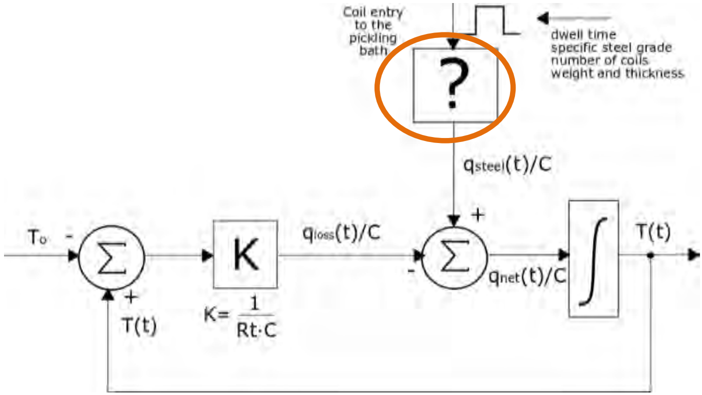
- Splitting the data to form a training dataset representative for the *qsteel*(t)/C heat flux triggered by the exothermic reaction of **each steel grade concerning the pickling stage**.

- *qsteel*(t)/C is standardized **per unit of weight and thickness**.

- Establish **zones of linear behavior regarding bath temperature ranges** for which the *qsteel*(t)/C heat flux is obtained.

- Input variables: number of coils introduced for a single pickling operation, dwell time, weight and thickness of the coil.

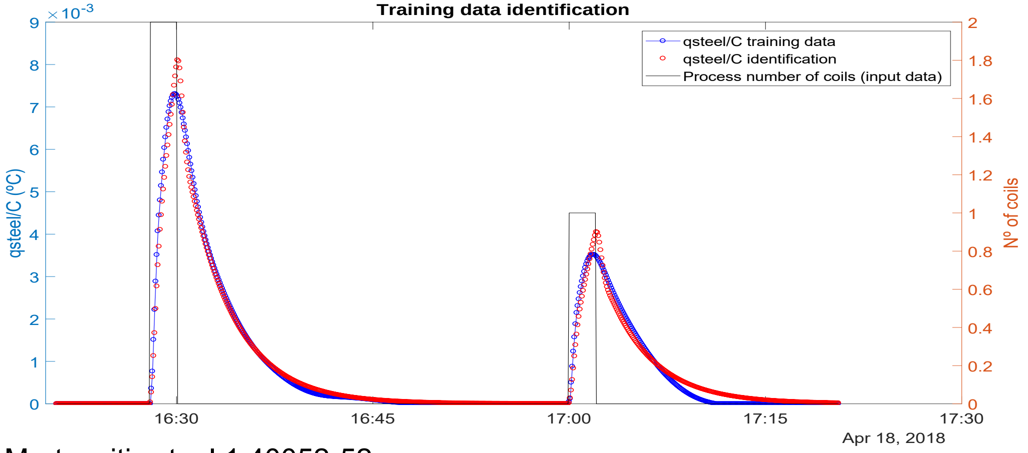
- Identification application: ARMAX model for the dynamics of the pickling process.



Model obtained for each steel and each pickling stage.

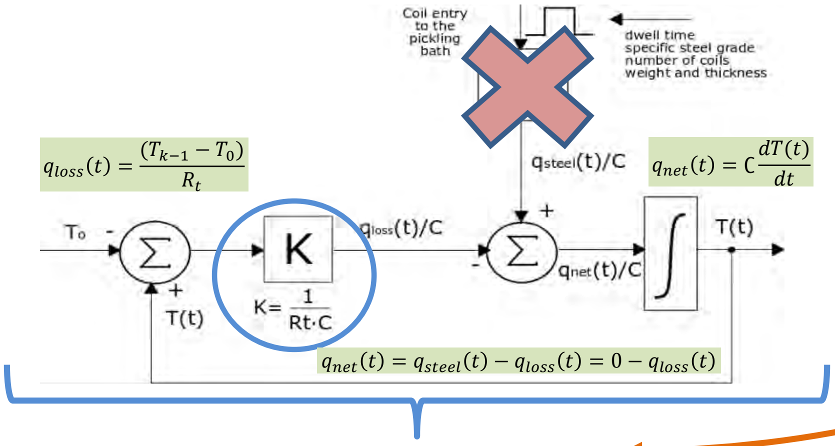
↓

Composed of a set of bath temperature ranges for which a transfer function is established.



Martensitic steel 1.40052-52
Stage 1 of pickling programmes 88 and 89

Cooling system dynamics



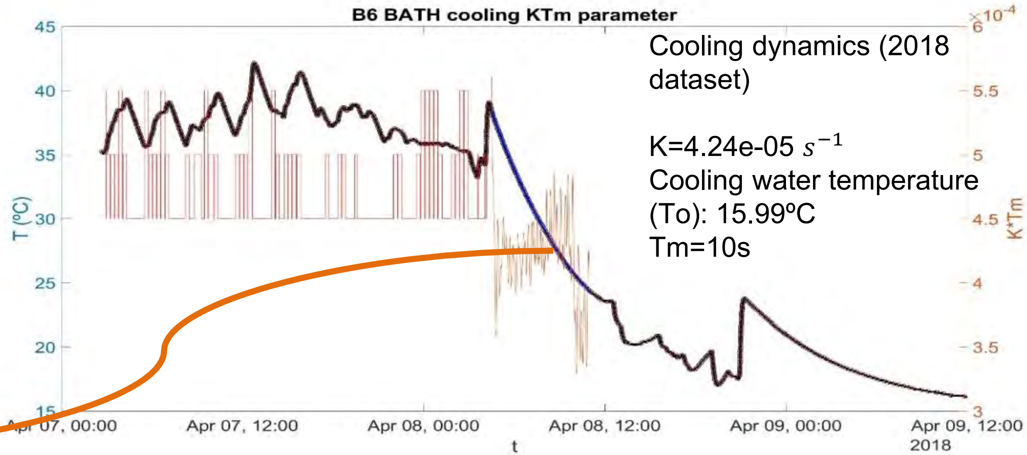
$$\frac{q_{loss}(t)}{C} = \frac{dT(t)}{dt} = K \cdot (T_0 - T_{k-1})$$

K parameter (constant) for the dynamics of the cooling system.

- K do not depend on To.
- Evaluates the performance of the cooling system (resistance and constant of the coolant fluid).
- Better cooling performance → ↑K

Affected by wear

↓K ↑Wear

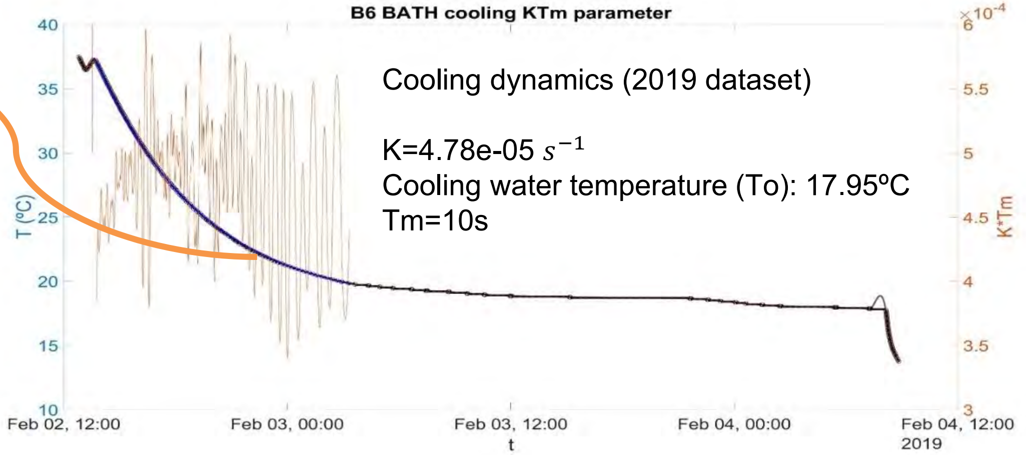


Cooling dynamics (2018 dataset)

K=4.24e-05 s^{-1}

Cooling water temperature (To): 15.99ºC

Tm=10s



Cooling dynamics (2019 dataset)

K=4.78e-05 s^{-1}

Cooling water temperature (To): 17.95ºC

Tm=10s

Development of the pickling programme management model

- Functions programmed in .m archives to obtain both the training data and the validation data. Variables established in matrix format and data vector.

- Scripts in .m archives to obtain heat flux distributions and training variables in order to get the transfer function (TF) models.

- Transfer function models obtained with ARMAX identification for each steel treated in each pickling programme stage (stored in .mat archives).

- .m scripts to carry out simulations and offline testing of the heat flux distribution and the temperature evolution for each combination of:

  - Coil characteristics: steel code, thickness and weight.
  - Pickling programme and stage of the pickling sequence.
  - Dynamics of the cooling system (K parameter).

Training data (datasets from March to June of 2018)

Validation data (datasets from January to March of 2019)

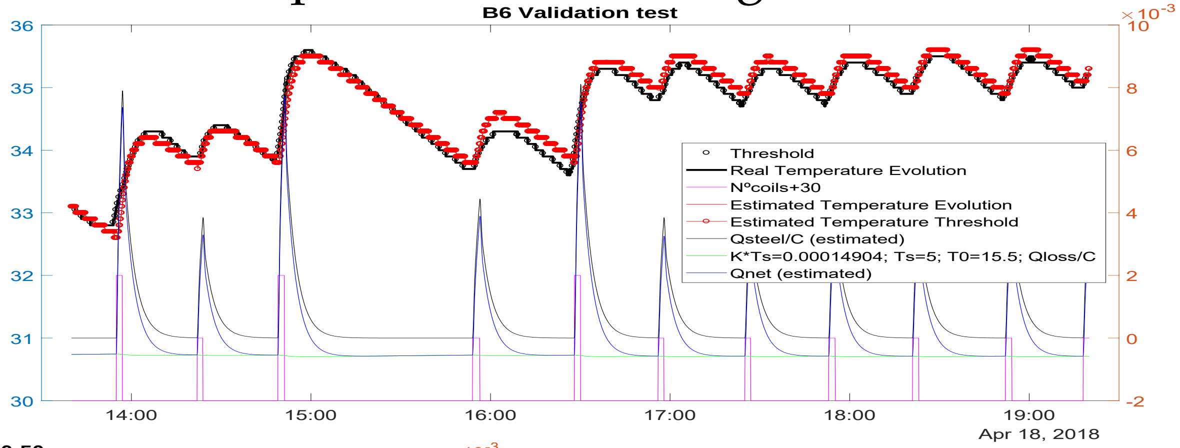
Offline-simulated tests and optimization investigations

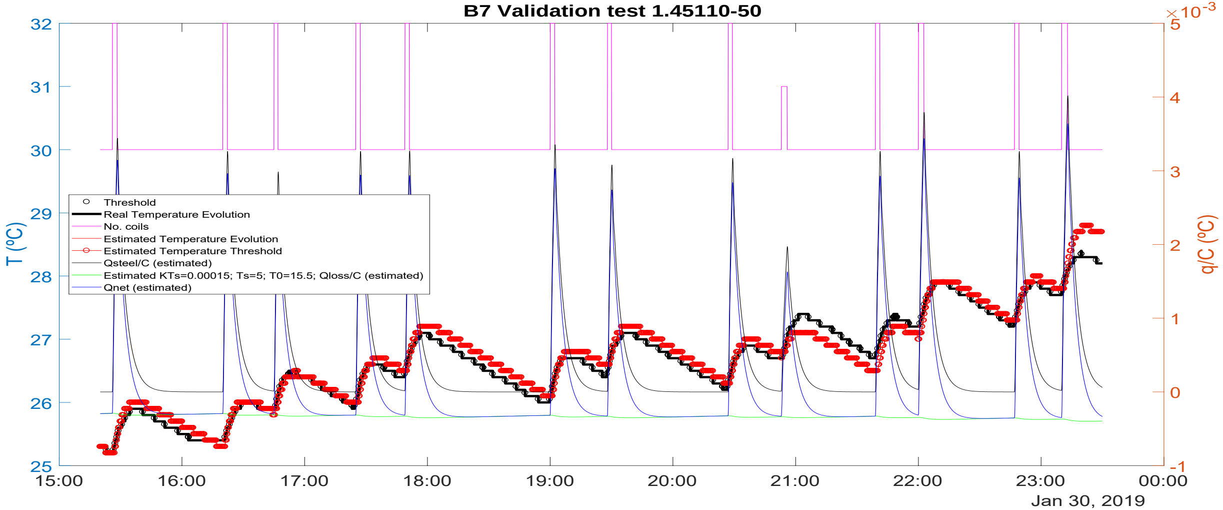
Martensitic steel 1.40052-52

Stage 1

TF in range between 30 and 35 ºC

Pickling programme 89





Martensitic steel 1.45110-50

Stage 1

TF in range between 25 and 30 ºC

Pickling programme 89

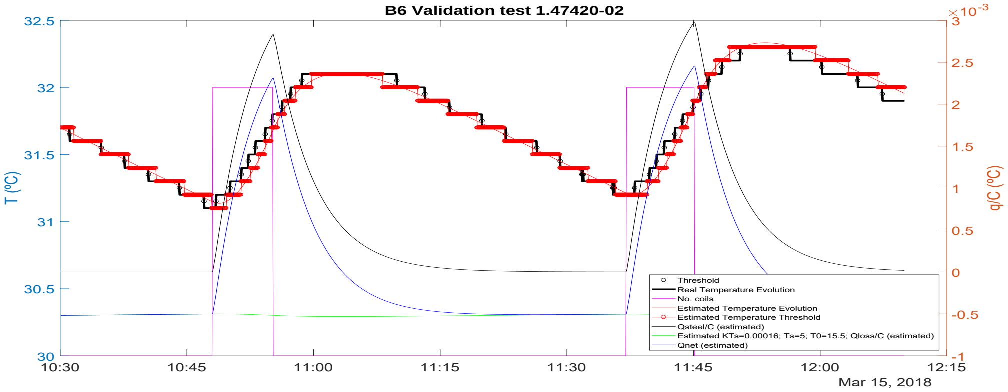
Offline-simulated tests and optimization investigations II

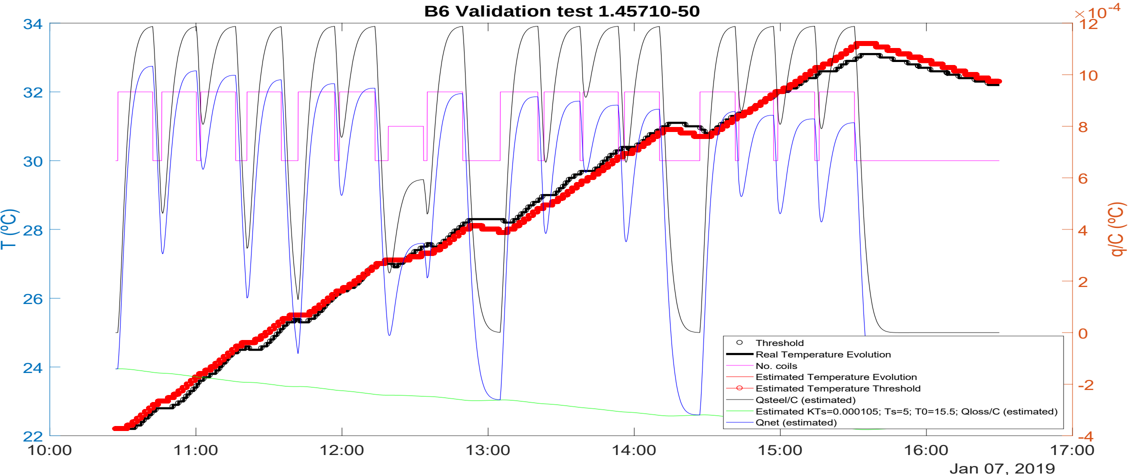
Ferritic steel 1.47420-02

Stage 1

TF in range between 30ºC and 35ºC

Pickling programme 40





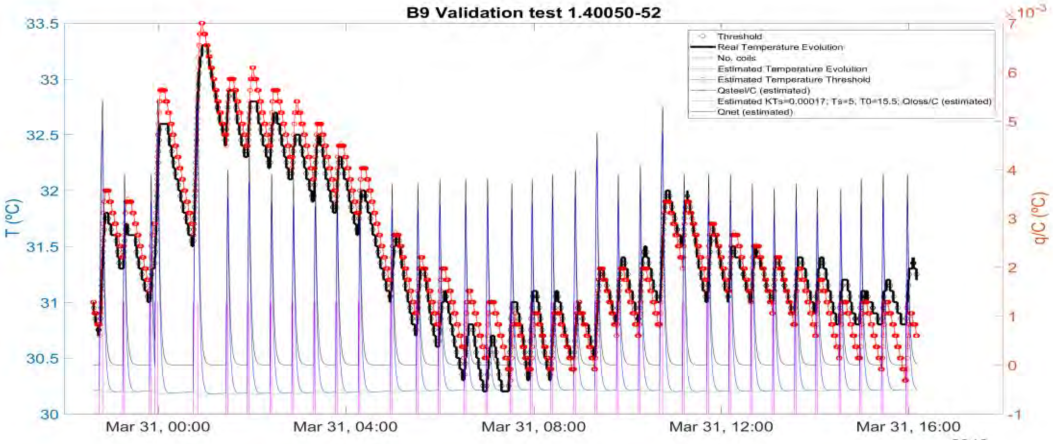
Austenitic steel 1.45710-50

Stage 1

TF in range between 20ºC and 30ºC

Pickling programme 23

Offline-simulated tests and optimization investigations III



Martensitic steel 1.40050-52

Stage 2

TF in range higher than 30ºC

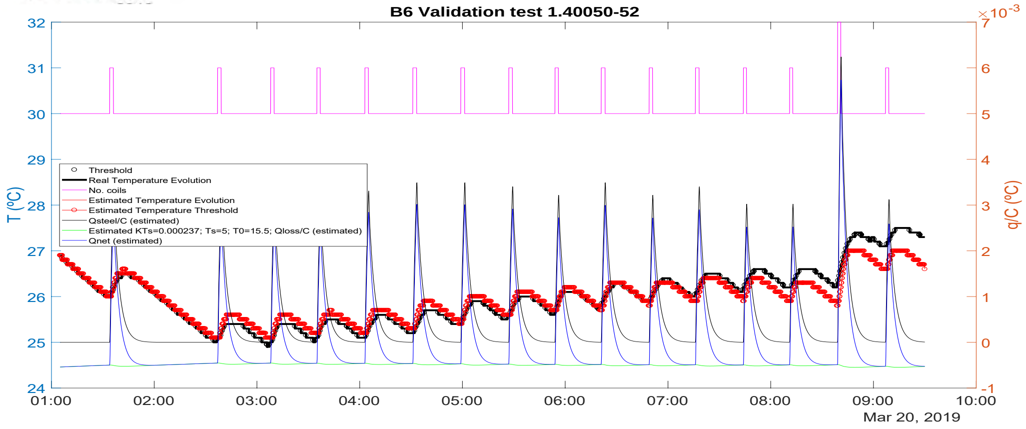
Pickling programme 88

Martensitic steel 1.40050-52

Stage 1

TF in range between 25 and 30 ºC

Pickling programme 88



Establishment of the platform for the online model

The online model (GUI application) is programmed under Matlab environment and can be run as a script (.m file).

- Functions and complementary scripts programmed in .m files (modifications must be carried out in Matlab environment).
- Transfer function models obtained with ARMAX identification for each steel established as .mat archives.
- Editable .xlsx file including the pickling programme characterization (BEIZPROGRAMM.xlsx).

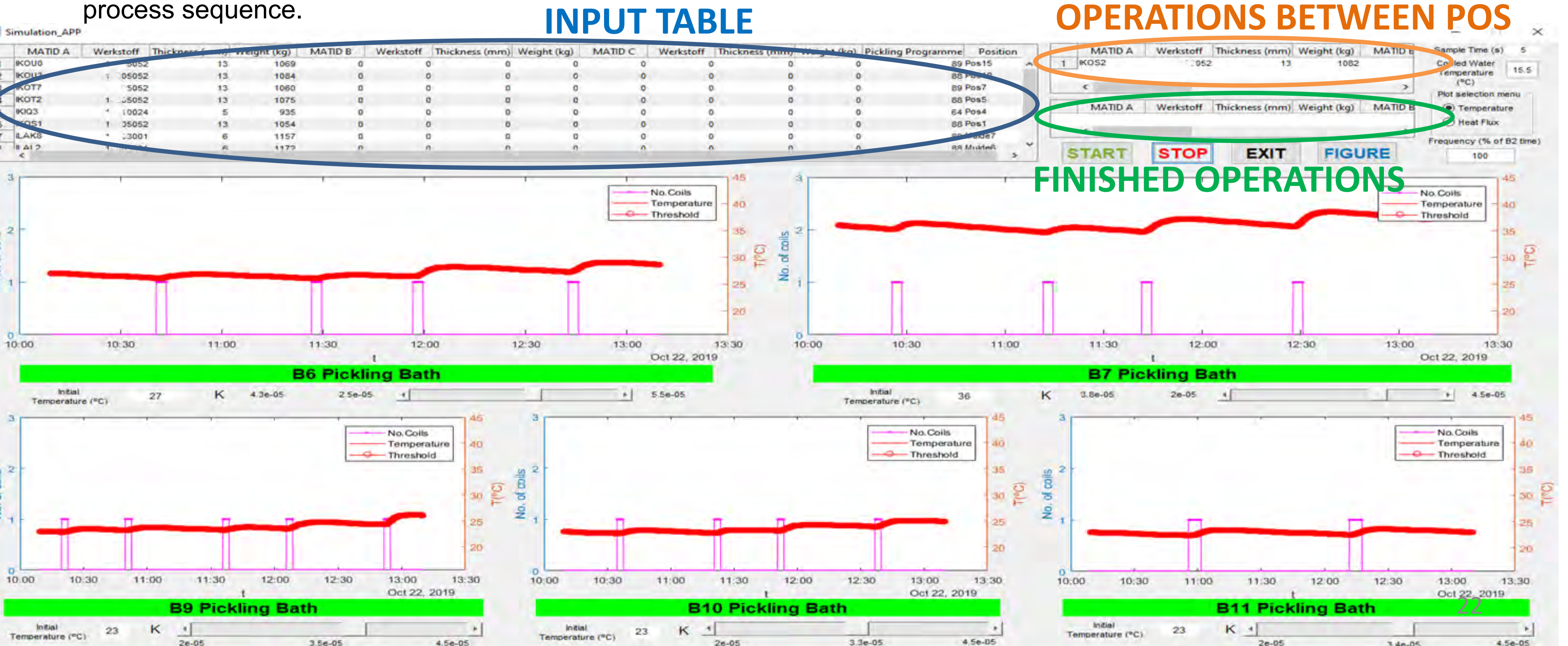
The GUI application can be run outside Matlab environment (standalone application).

- Executable file .exe included in the same folder as the model files (.mat) for the stainless steels and the BEIZPROGRAMM.xlsx.
- User-friendly graphical interface with multiple options to simulate and evaluate the evolution of the temperature due to a pickling sequence.

GUI versions for the pickling management tool

Supervision version

- Graphical User Interface for the continuous supervision of the pickling process concerning data from the database system (refreshes every minute to synchronize the database system).
- Predictions for the evolution of the temperature of the pickling baths and the heat flux distribution generated by the pickling process sequence.



GUI versions for the pickling management tool

Supervision version

- The frequency between single operations can be increased or reduced percentage-wise.

- The figures plotted in the user interface can be changed between Temperature (temperature evolution) and Heat Flux (heat flux distribution).

- The water temperature of the cooling system can be modified regarding the current necessities.

- The temperature of the pickling baths is captured and actualized from the database system every minute, and it is established as the initial temperature for the simulations.

- The efficiency of the cooling system (K parameter) can be increased or decreased regarding the current necessities for each pickling bath.

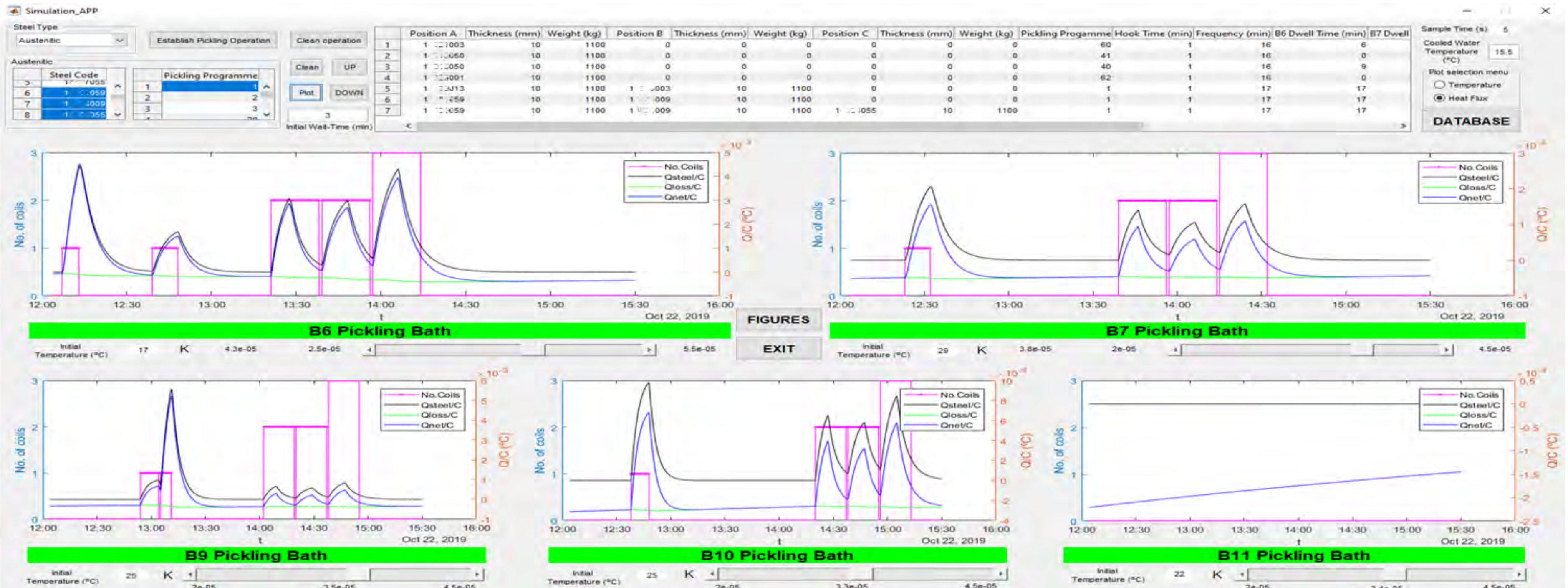
- The pickling process sequence is established avoiding overlaps between processes.

- The simulation avoids operations which are already in positions after pickling baths and does not consider stages of the pickling already carried out.

GUI versions for the pickling management tool

Logistic version

- Graphical User Interface to manage the logistics of an integral pickling sequence.
- Predictions for the temperature of the pickling baths and the heat flux distribution generated by a pickling sequence.
- The pickling sequence is obtained from the database system and can be modified (all variables in the input table are editable, and processes can be also included from the user interface selection menu).



GUI versions for the pickling management tool

Logistic version

- The figures plotted in the user interface can be changed between Temperature (temperature evolution) and Heat Flux (heat flux distribution).
- The cooled water temperature of the cooling system can be modified regarding the current necessities.
- The temperature of the pickling baths is captured from the database system when the PLOT button is pressed, and it is established as the initial temperature for the simulation.
- The efficiency of the cooling system (K parameter) can be increased or decreased regarding the current necessities for each pickling bath.
- The pickling process sequence is established avoiding overlaps between processes. The simulations are done considering the whole information contained in the input table and maintaining the operation order established.
- Press PLOT button to carry out the simulation of temperature evolution and heat flux distribution regarding the sequence and the information established in the input table.

GUI versions for the pickling management tool

Additional characteristics

- New steel models can be added and recognized by just including them in the application folder (.mat archives).

- Pickling programmes can be modified or created by editing the file “BEIZPROGRAMM.xlsx” (respecting the format and proportions of the document).

- When opening both applications, the connection to the database system is evaluated, delivering error messages when the connection fails.

- After the connection to the database system is successful, the file “BEIZPROGRAMM.xlsx” must be selected and charged to the application (a window will pop up for its selection, delivering error messages if the file selected is not “BEIZPROGRAMM.xlsx”).

Thank you for your attention!

Optimisation of pickling process control and management by model-based simulation tools

University of Oviedo
Iván Machón González

13th of November 2019, Düsseldorf

MACO-PILOT

Sensor material corrosion investigations and sensor lifetime estimation

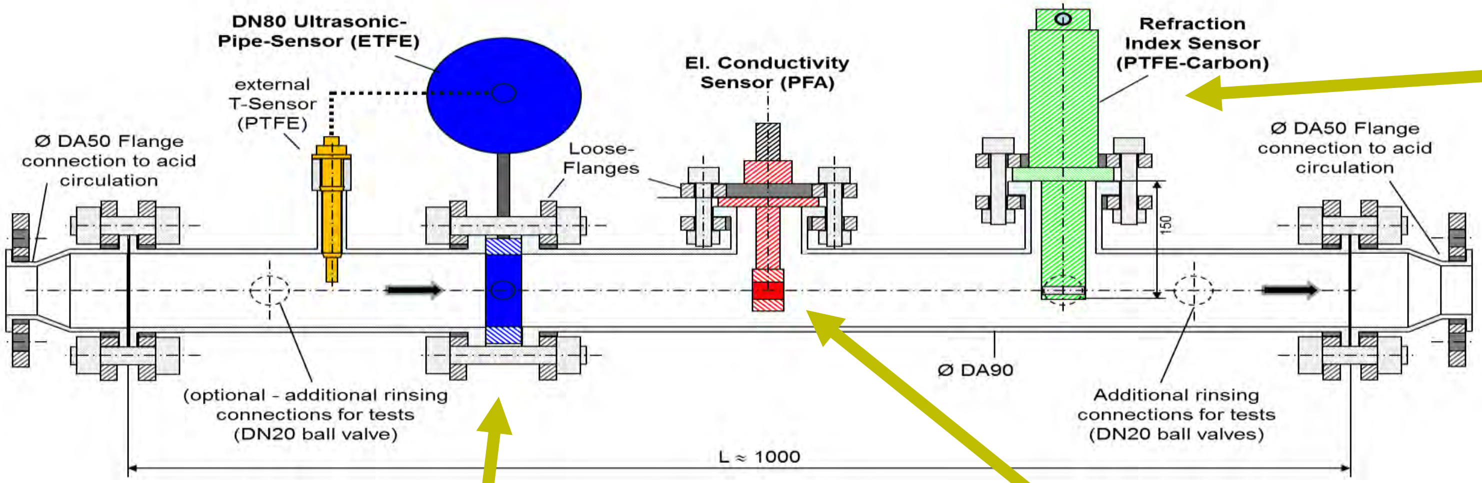
Jonas Engblom, Karin Jacobsson

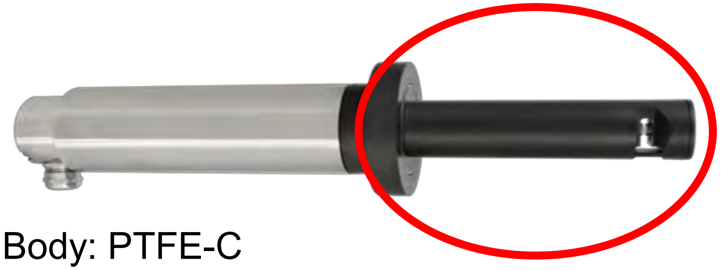
November 2019

RISE Research Institutes of Sweden

DIVISION
ENHET

MACO Pilot





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

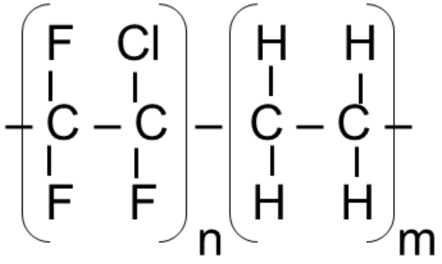
Body: EFTE coated steel
Temp sensor: PTFE

Body: PFA coated steel
Flange: PTFA

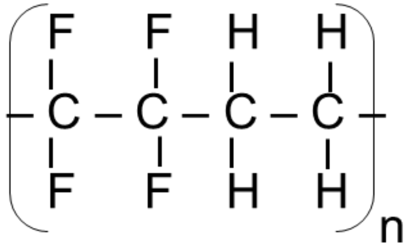
Fluoroplastics

- 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

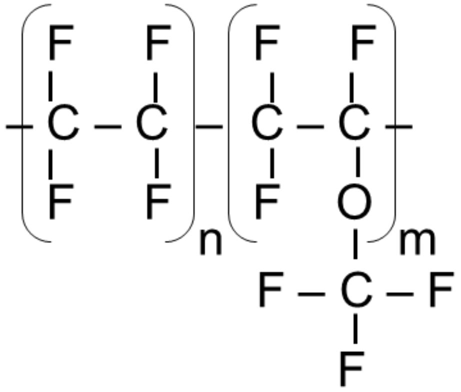
- ECTFE



- EFTE



- PFA

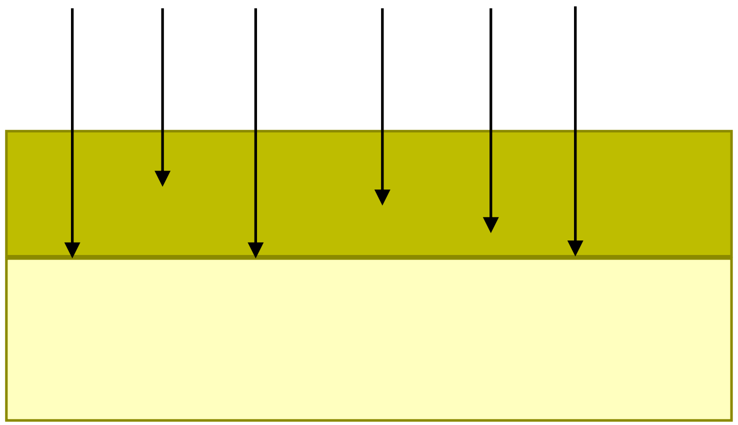


HOWEVER…

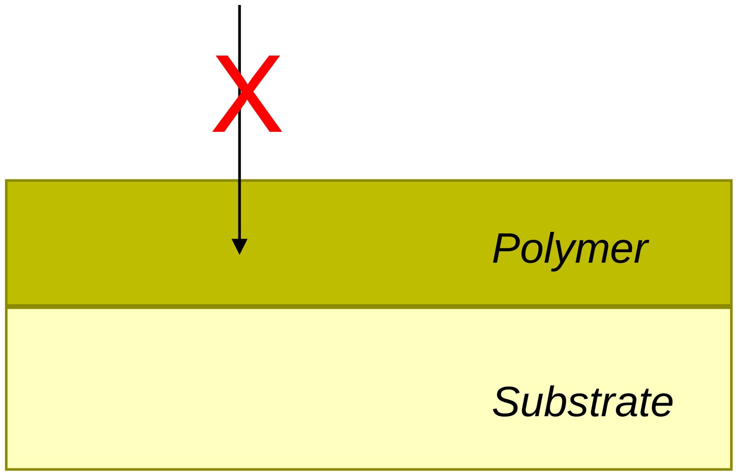
Plastics are permeable to small molecules

Ions do not permeate into the polymer

O_2, HF, HNO_3, NO_x, H_2O



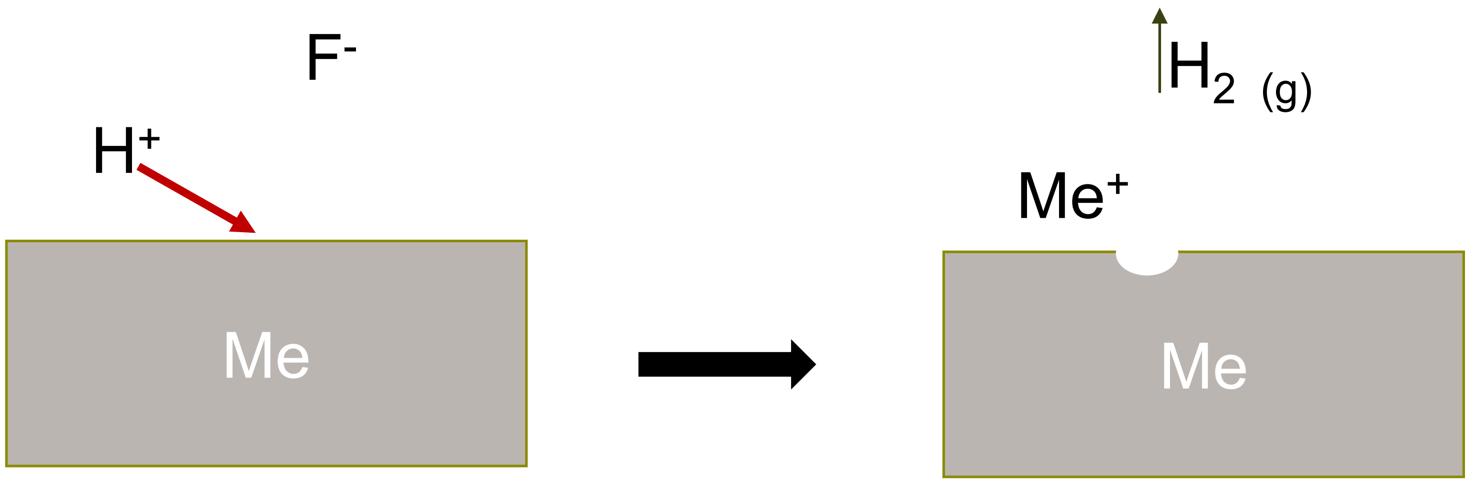
F^-, H^+



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

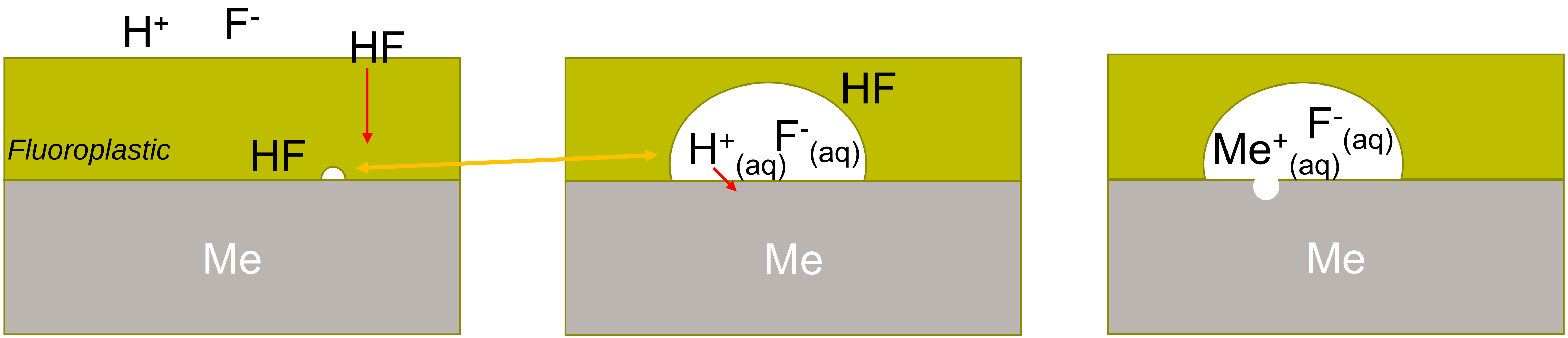
Corrosion of metals in acids

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

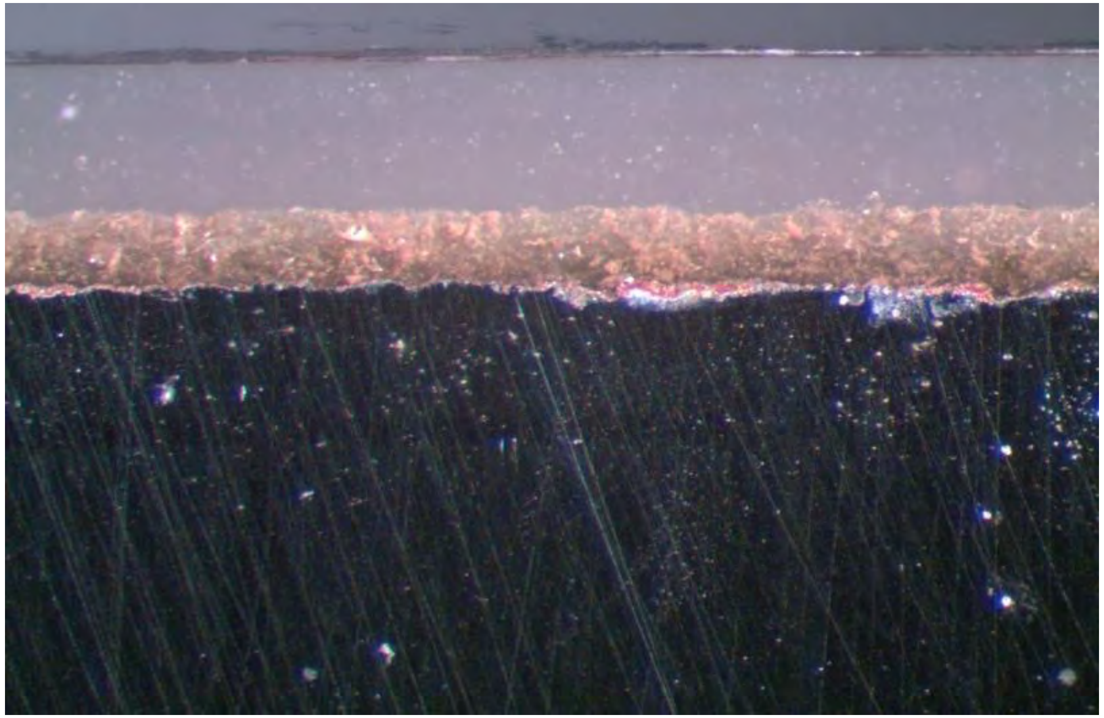


With imperfect polymeric coating

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

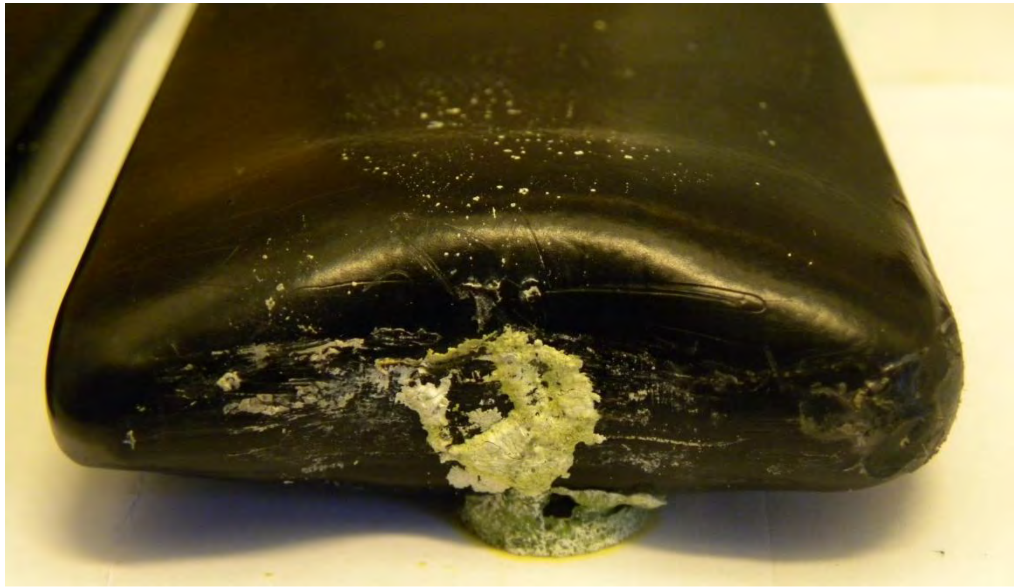
What happens when the penetrating acids reaches the interface between the steel and the coating?

- 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

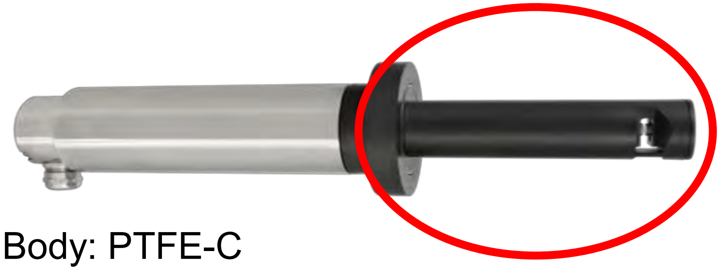
Another sensor with the same coating had a lifetime of 5.5 years

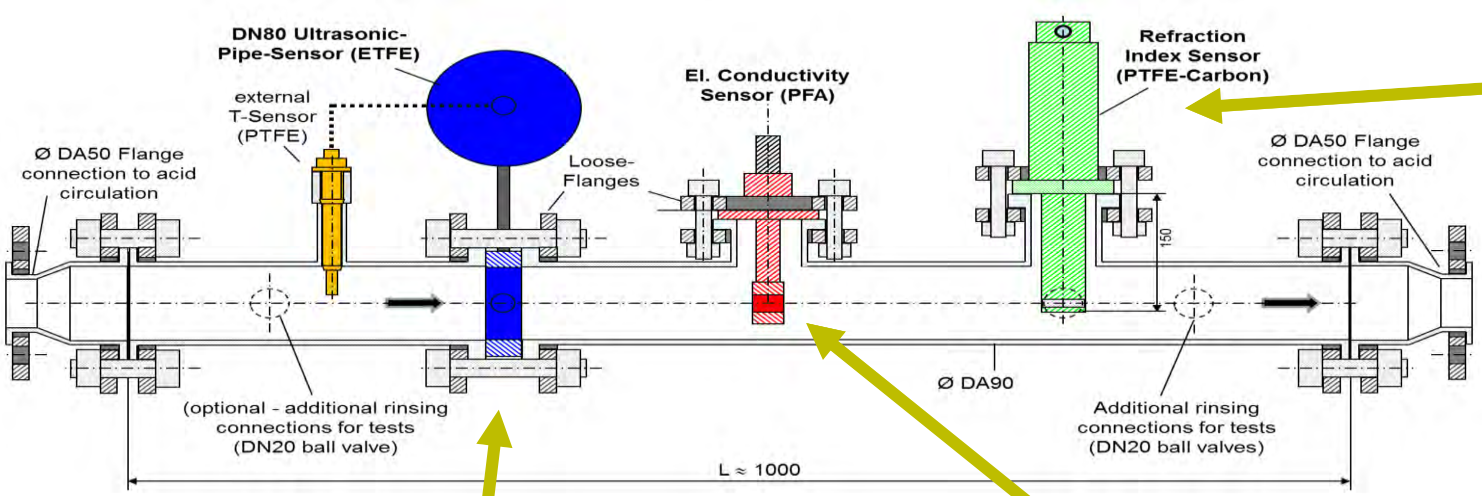
One major difficulty in exposing coated samples to study the diffusion is that there is a risk of penetration through holes in the coating. In this example at the point where it was hanging during the coating process



Task 4.3:

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





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

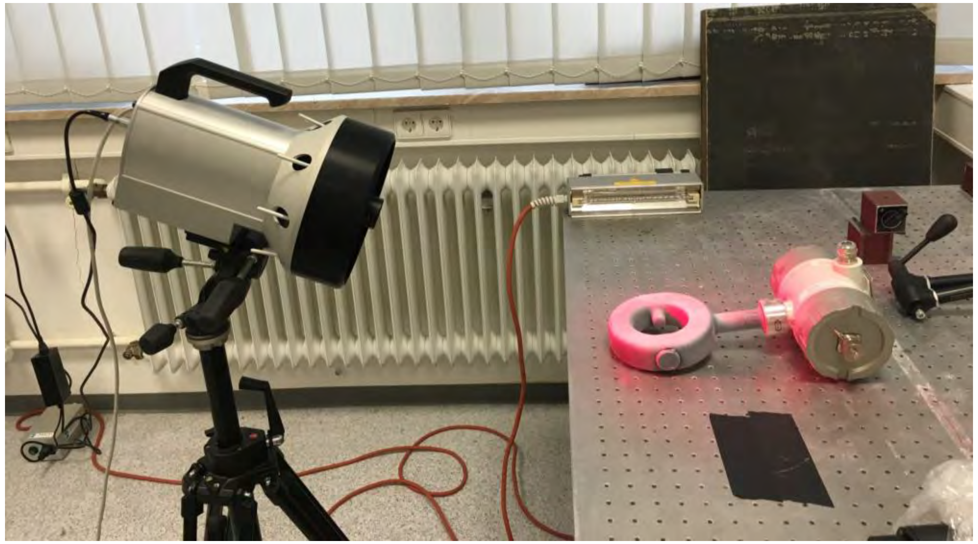
Body: EFTE coated steel
Temp sensor: PTFE

Body: PFA coated steel
Flange: PTFA

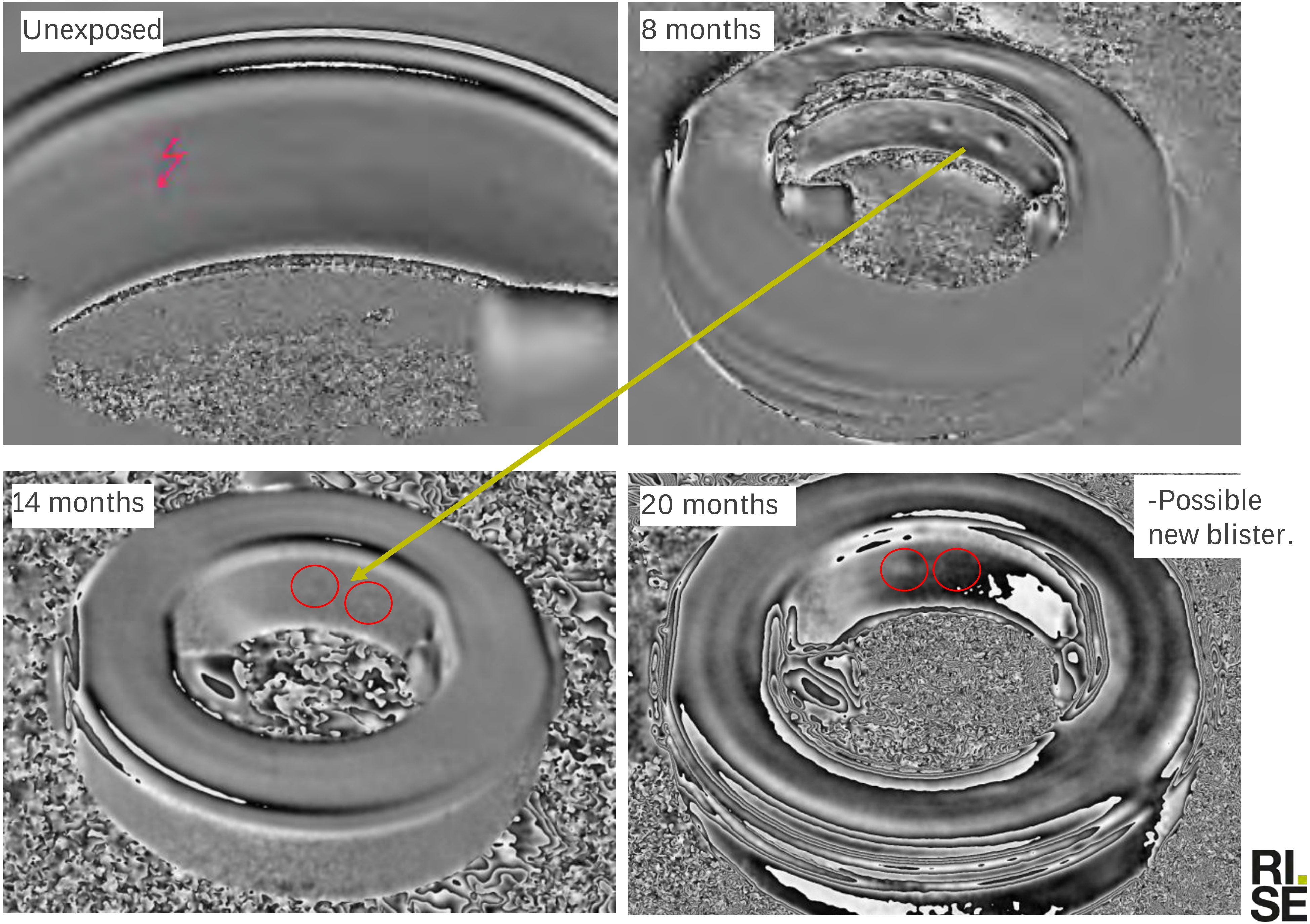
- Four sensor packs have been installed at four on-site locations.

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

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

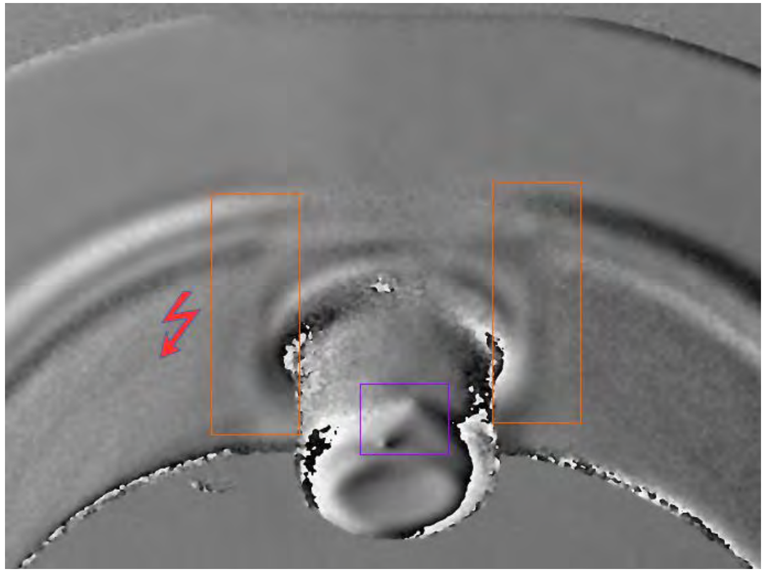


Pickling line, sensor 1

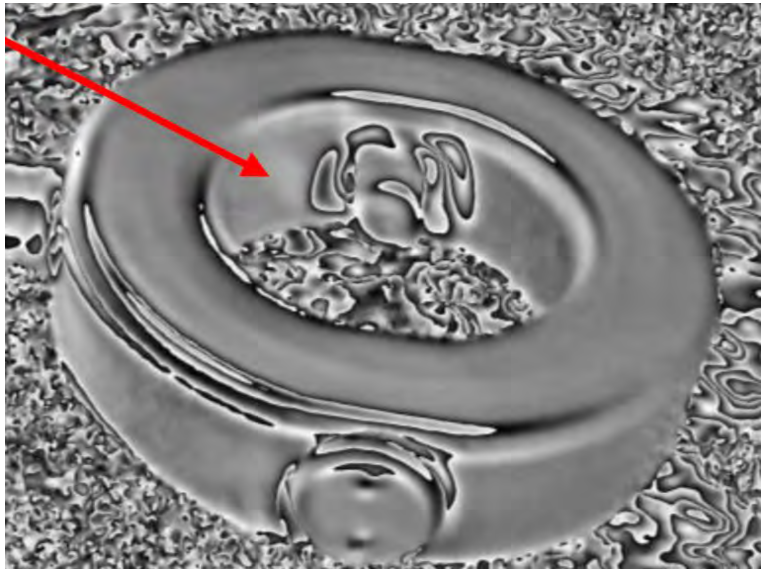


Sensor 2 exposed in pickling line

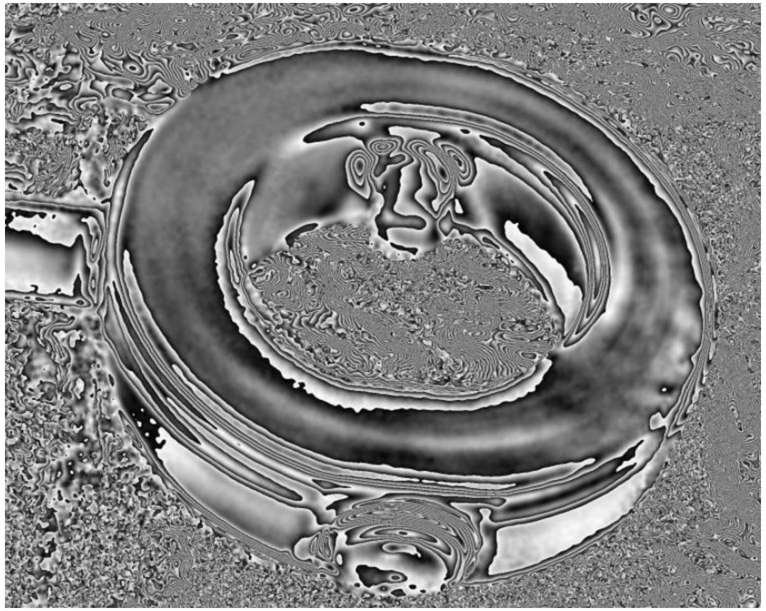
Unexposed



14 months
-possible delamination around head.

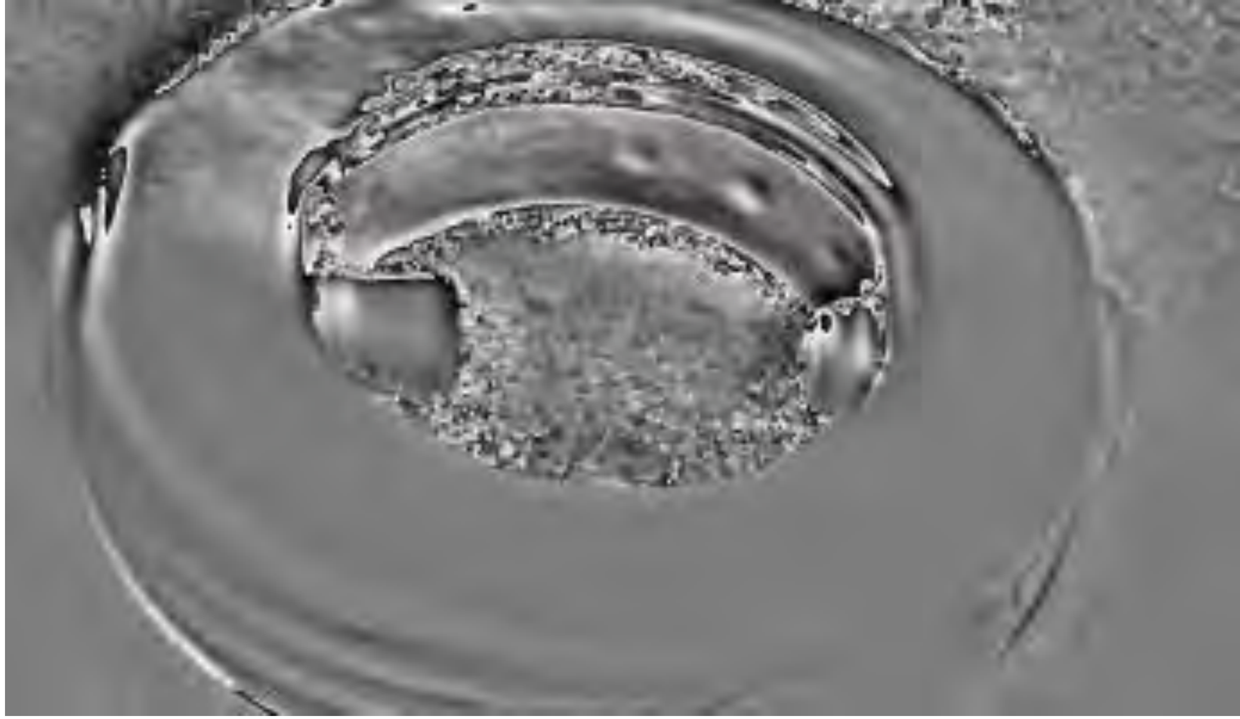


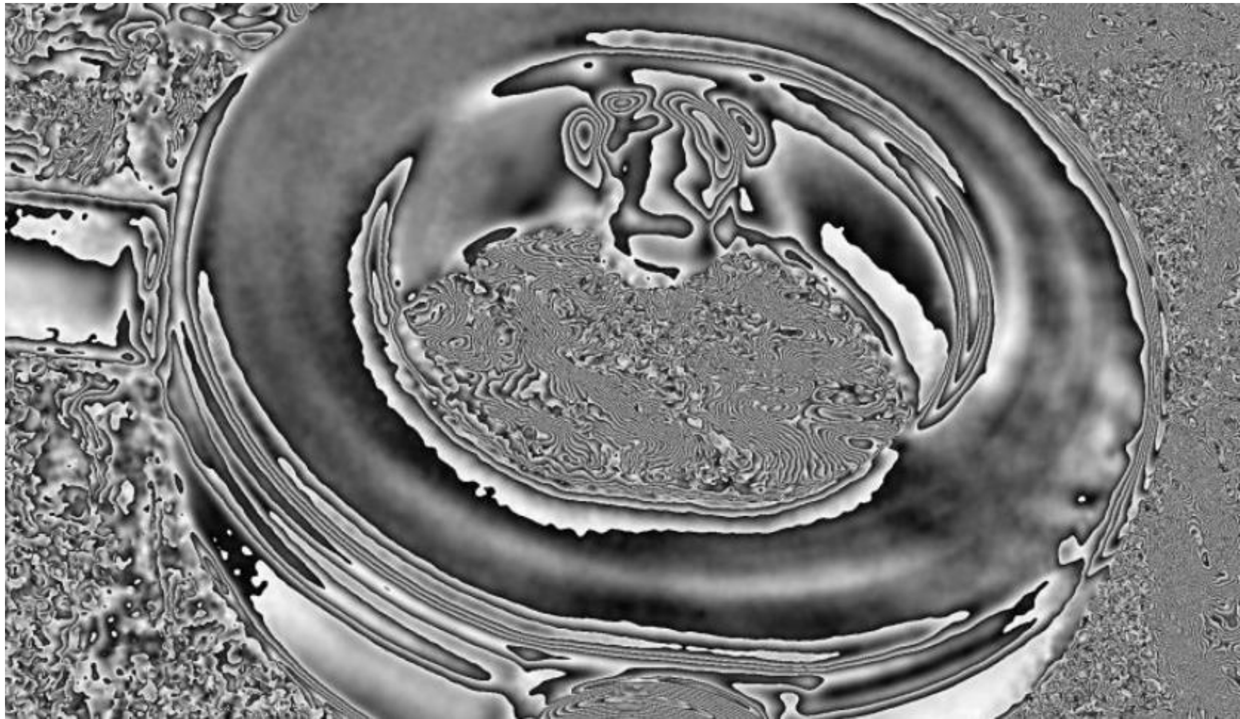
20 months
-possible growth of delamination around head.



- 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.

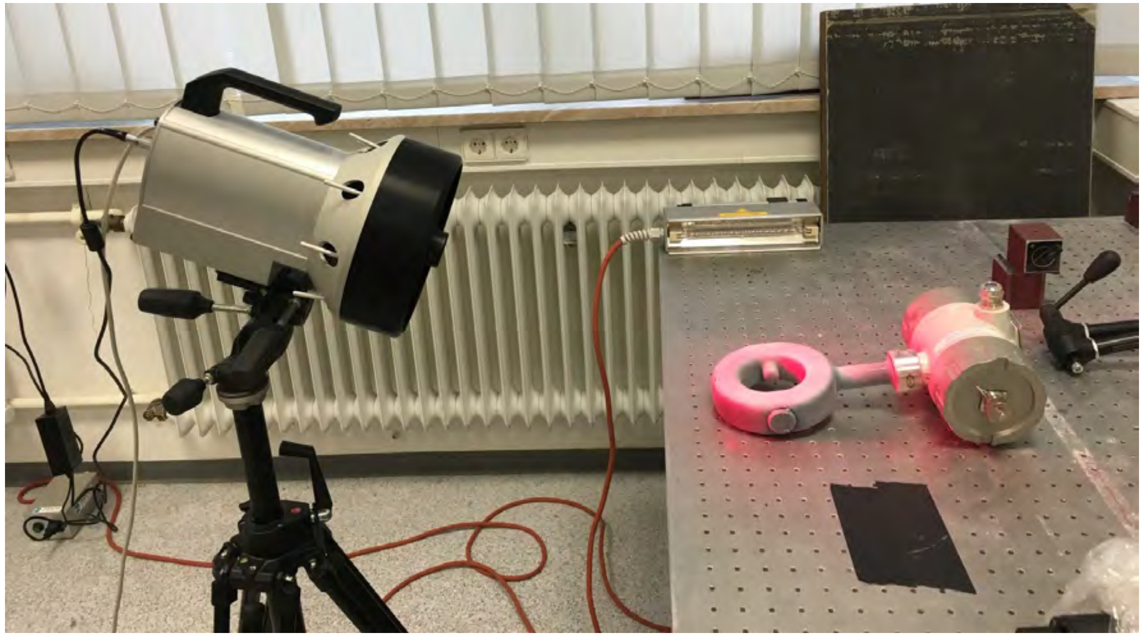
- By constructing a double lid, where the bottom layer seal the jar so it retains the acid, and the top layer is taking the load, a successfull design was achieved.

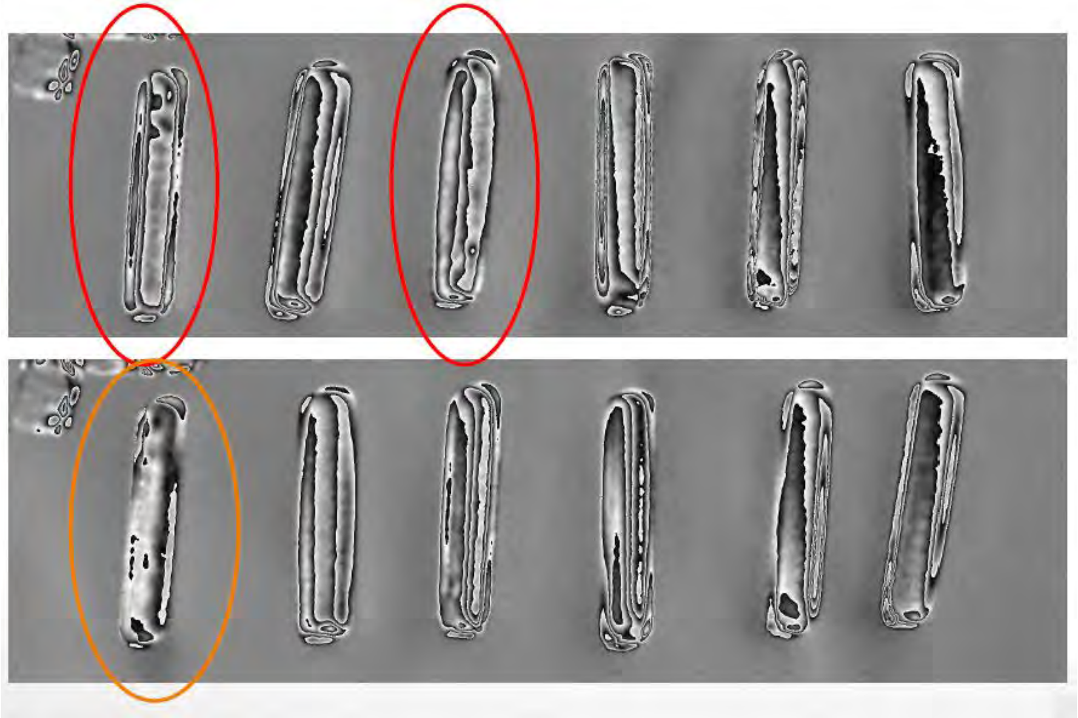
  If acid were to escape from the sealing layer, there is a ”ventilation crevice” between the layer, to prevent the acid from entering the threading.

Investigation of exposed pins

- 192 pins have been exposed

- LASER Shearography indicated delamination of varying degree on 30 pins (16%)

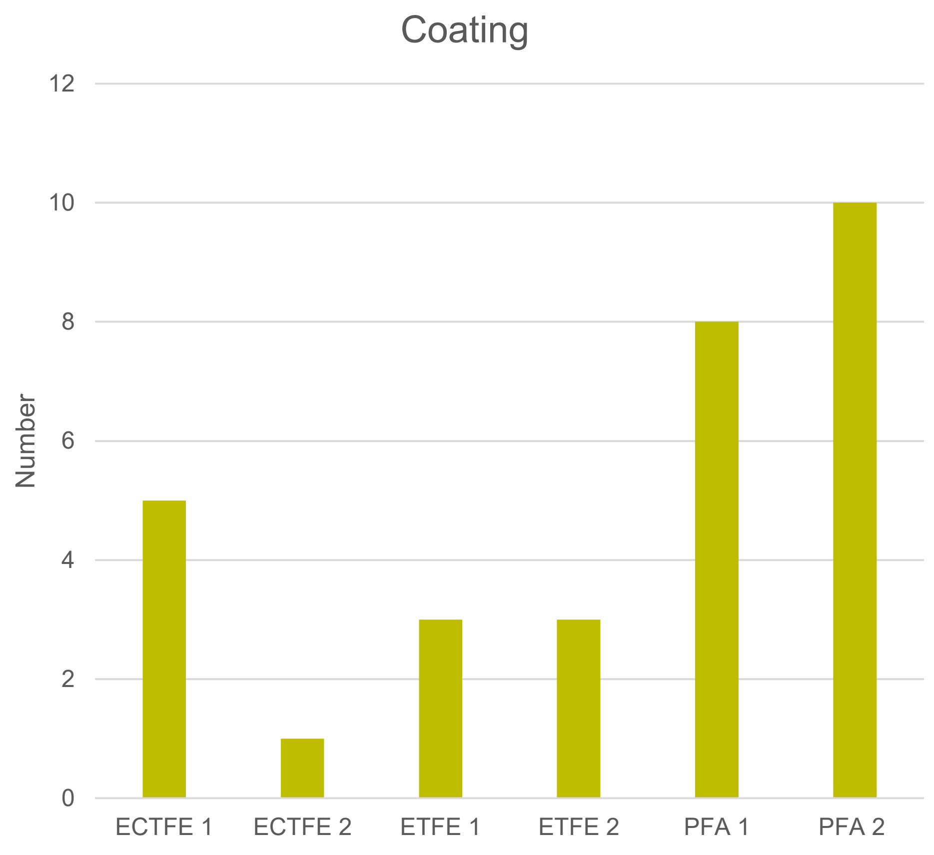




Distribution of the delaminated pins - Coating

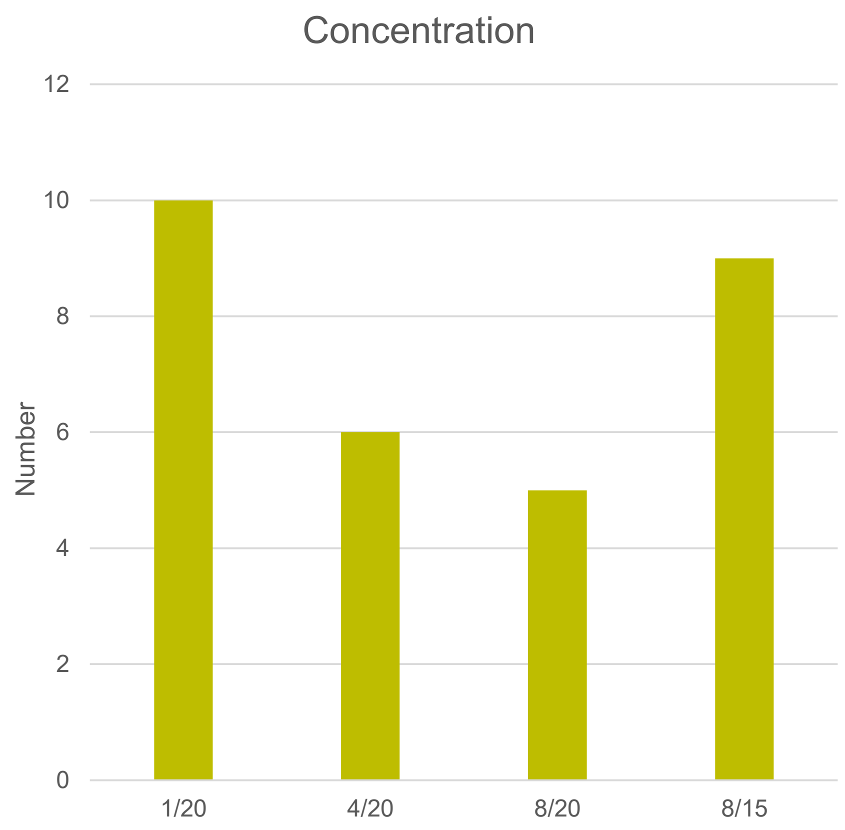
- 6/30 (20%) ECTFE
- 6/30 (20%) ETFE
- 18/30 (60%) PFA

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



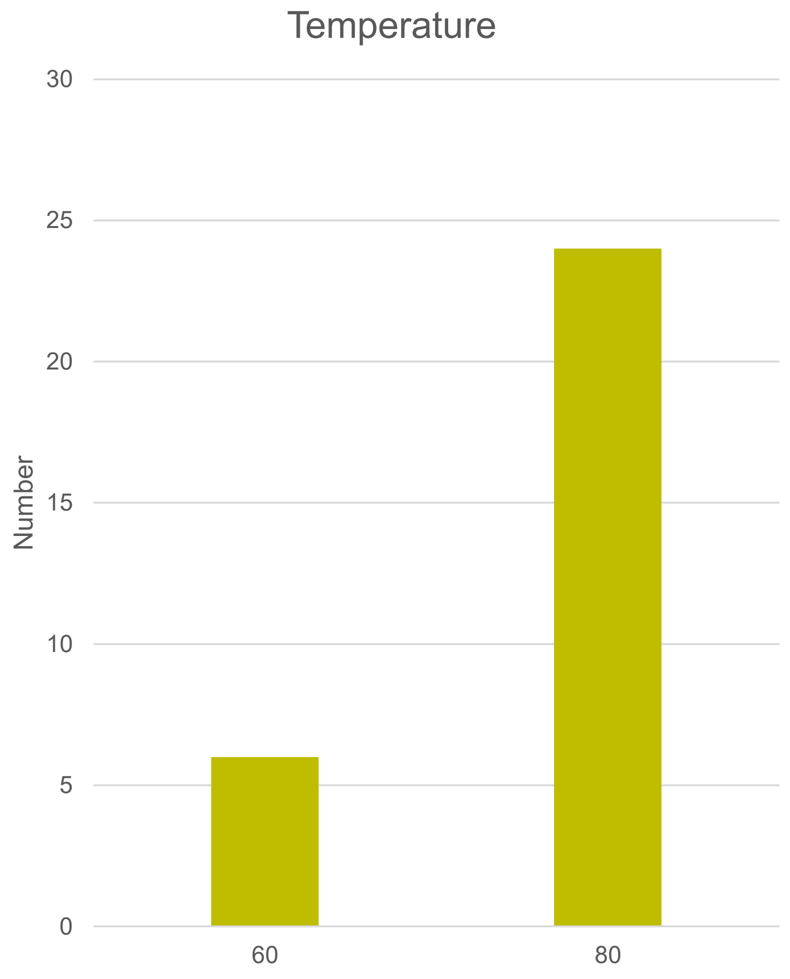
Distribution of the delaminated pins - Concentration

- 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



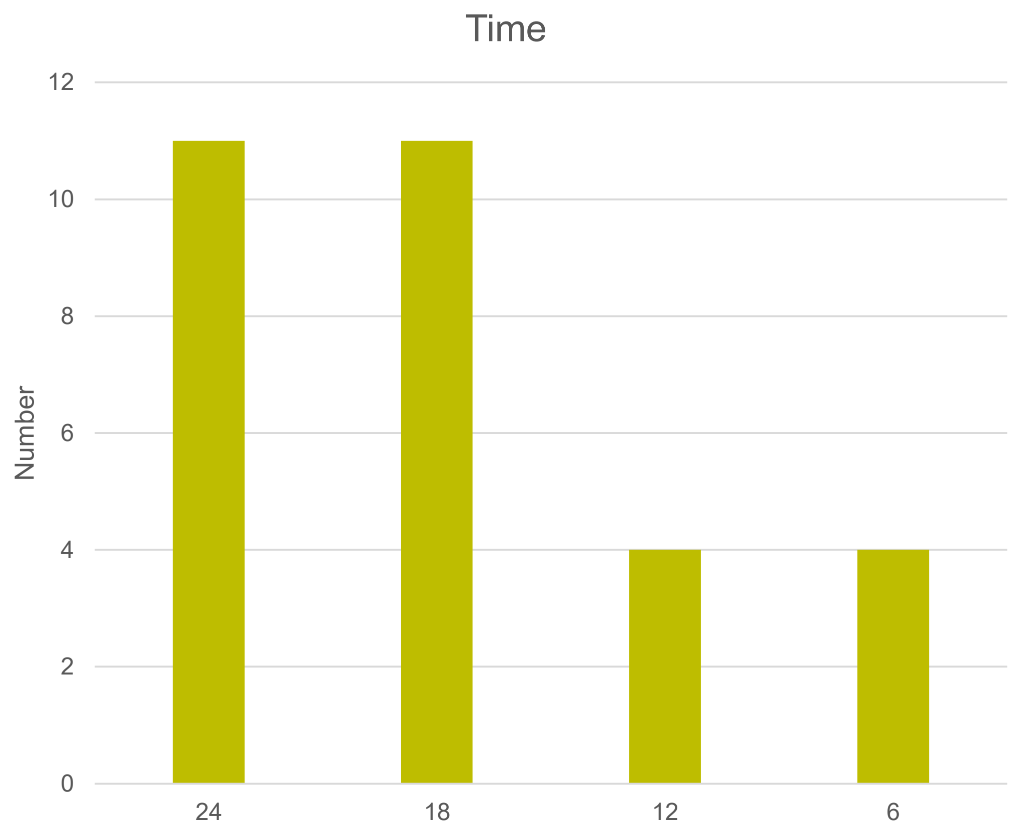
Distribution of the delaminated pins - Temperature

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



Distribution of the delaminated pins - Time

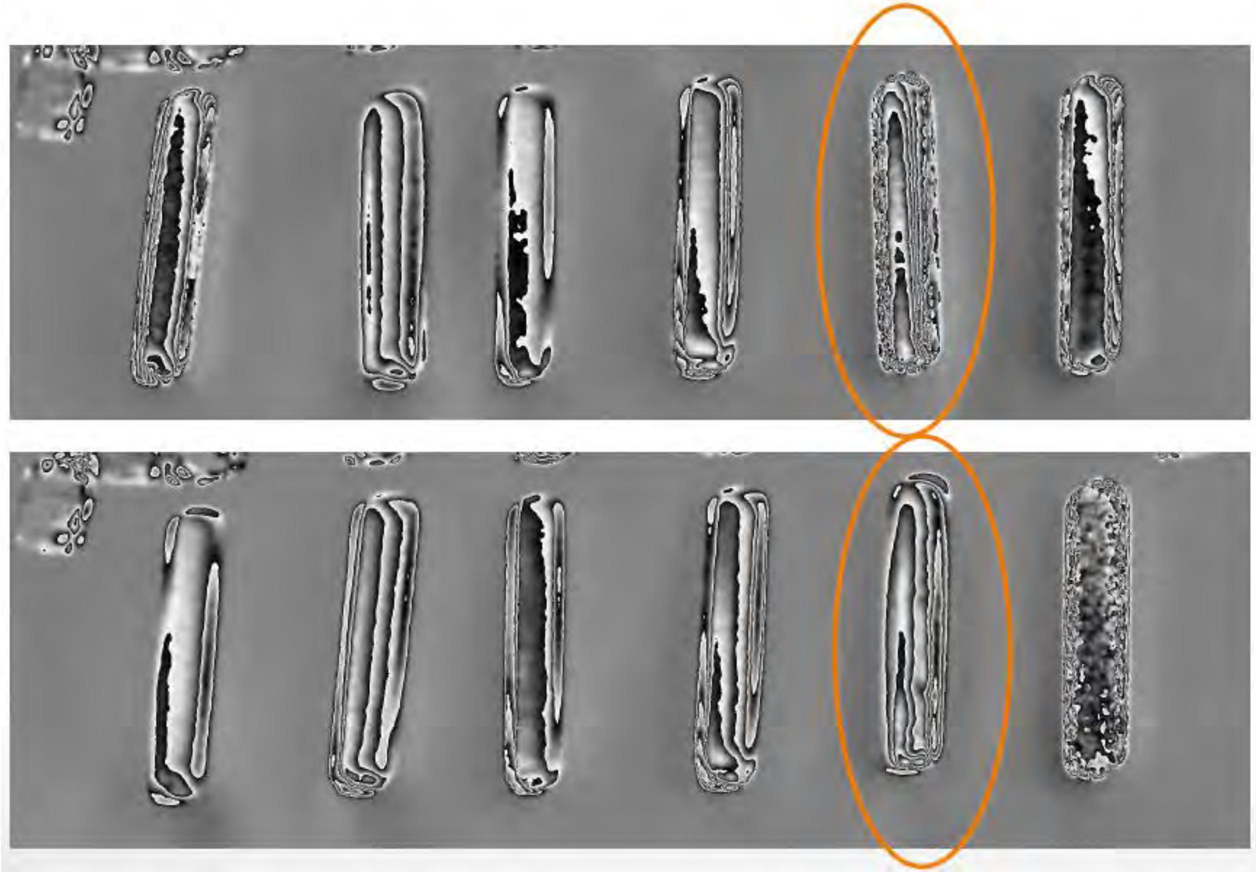
- 11/30 (37%) 24 months
- 11/30 (37%) 18 months
- 4/30 (13%) 12 months
- 4/30 (13%) 6 months



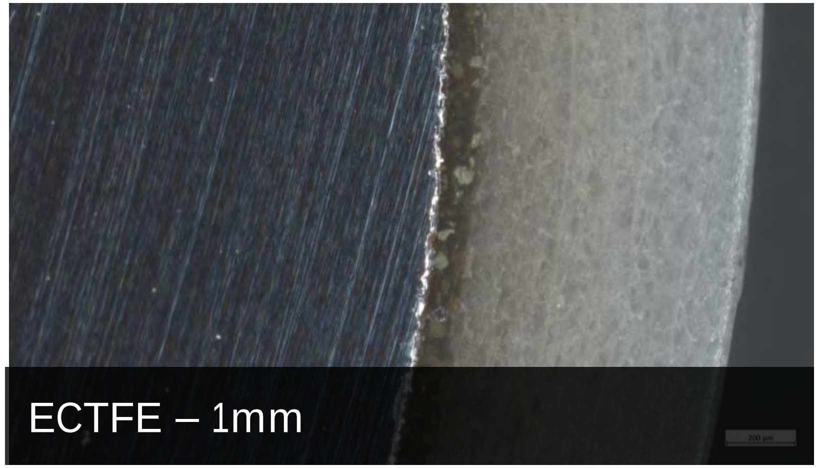
Validating LS – Jar 28

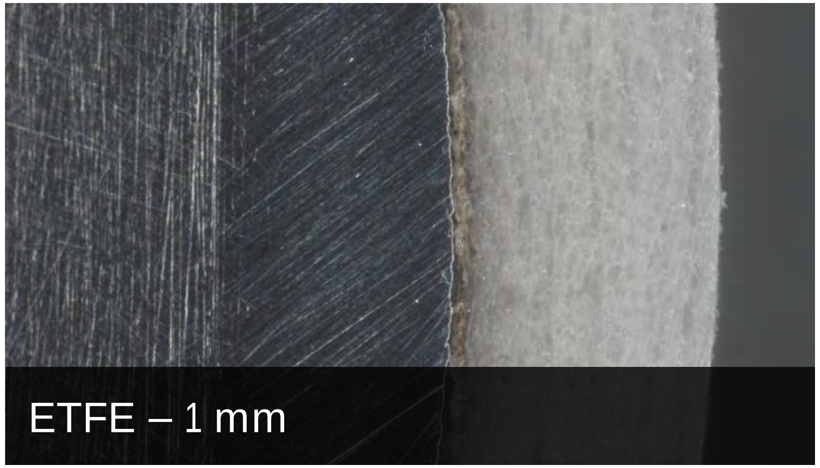
- 8/15
- 60ºC
- 6 months
- LS indicated only one delamination:

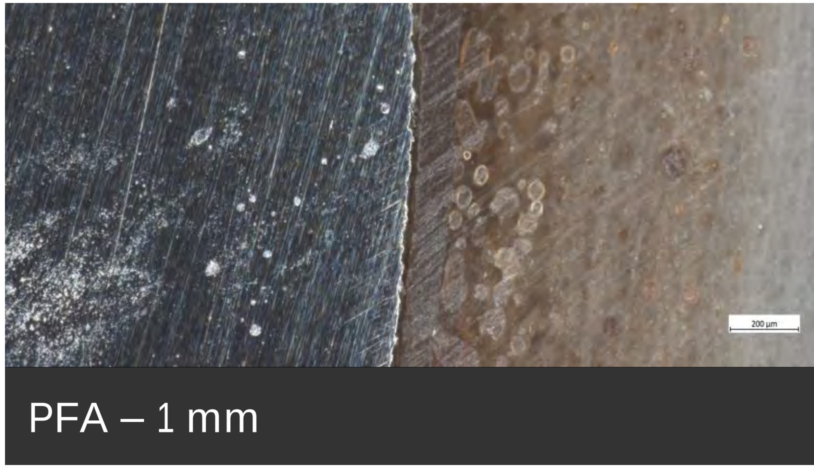
  28-5 (PFA 1 mm)

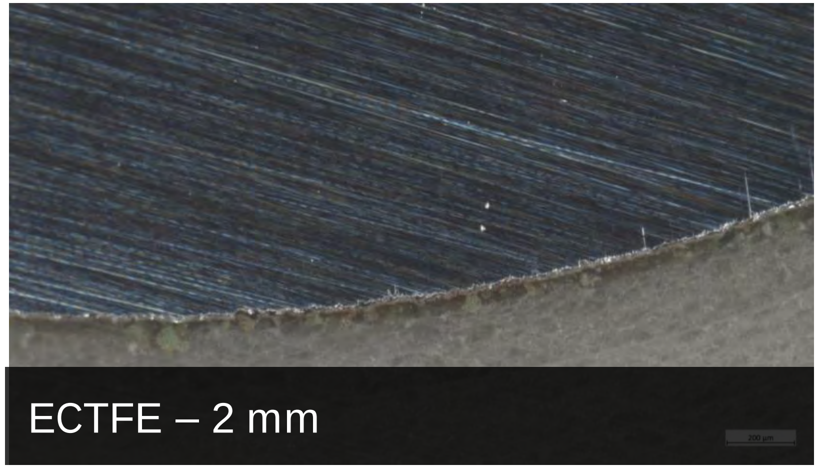


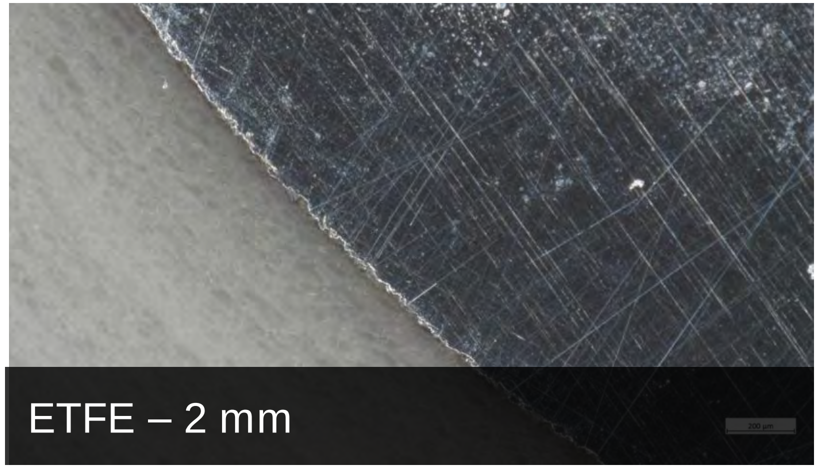
Cross sections of Jar 28

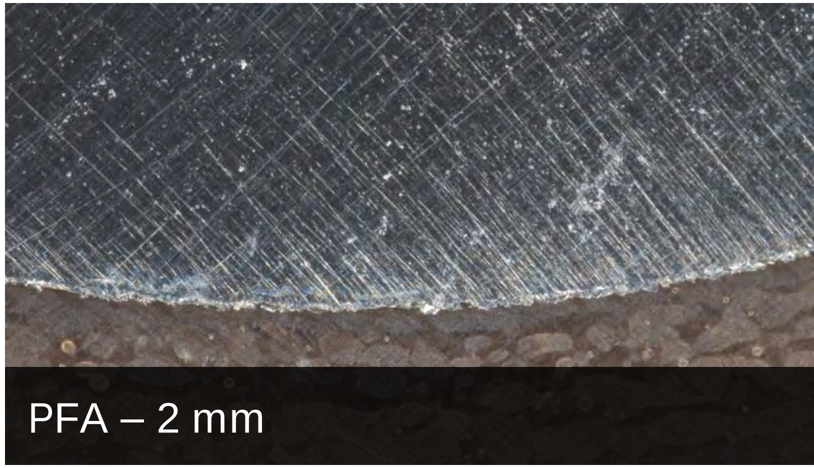

ECTFE – 1mm


ETFE – 1 mm


PFA – 1 mm


ECTFE – 2 mm


ETFE – 2 mm


PFA – 2 mm

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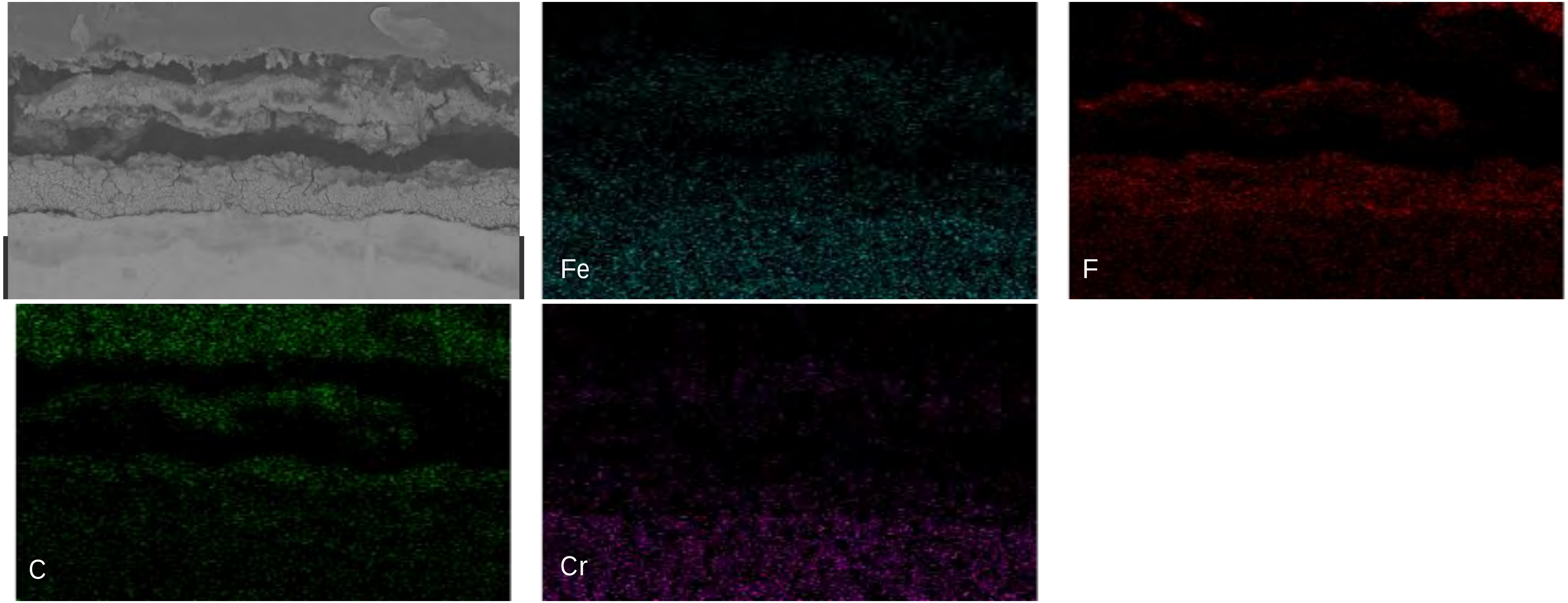
SEM/EDS of PFA delamination



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.

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THANK YOU!

QUESTIONS?

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Polymers in Corrosive Environments