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# Corrosion Monitoring of 304L Stainless Steel in Nitric Media using Electrical Resistance Probe in Intergranular Corrosion Mode

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DE LA RECHERCHE À L'INDUSTRIE

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# CORROSION MONITORING OF 304L IN NITRIC MEDIA USING ELECTRICAL RESISTANCE PROBE IN INTERGRANULAR CORROSION MODE

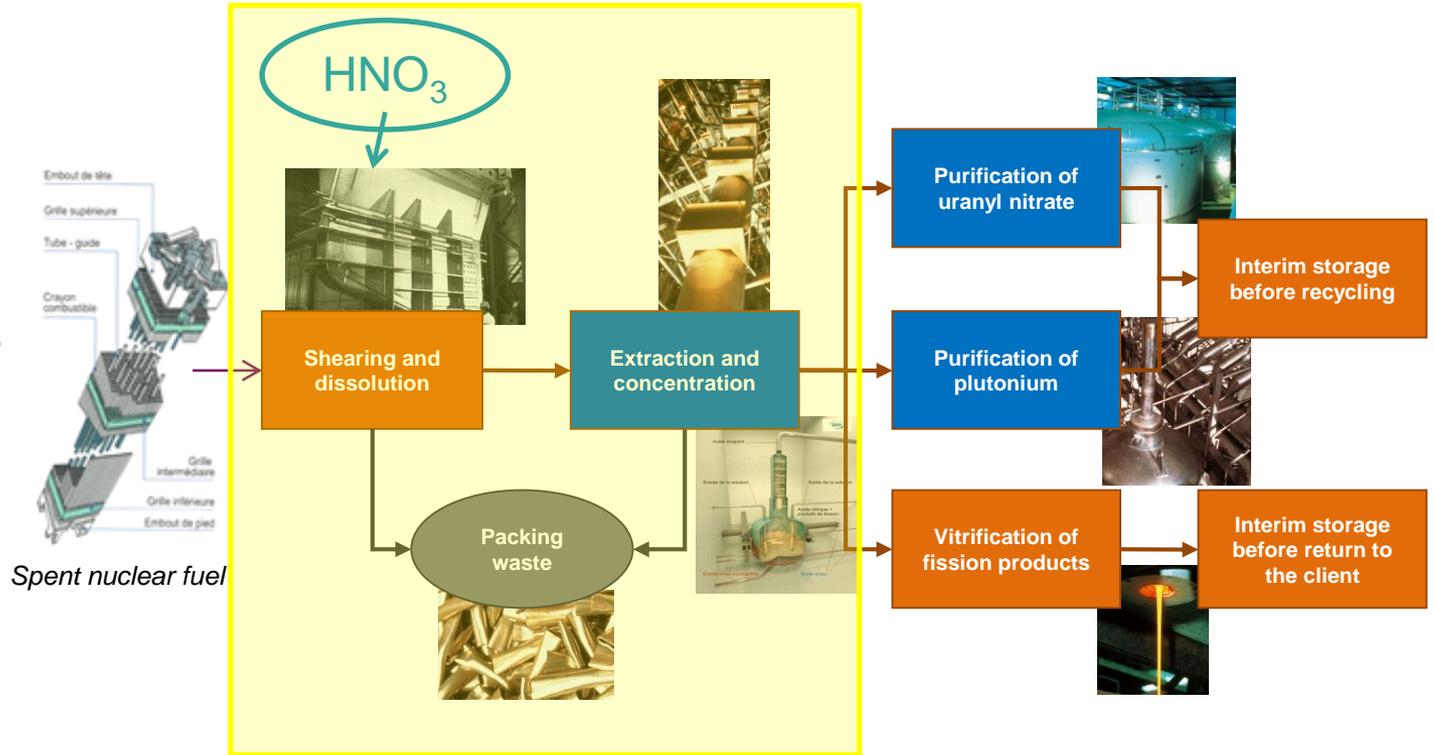
S. Bosonnet; B. Gwinner; A. Luangxay; K.Ginestar; R.Robin

NON-AQUEOUS CORROSION LABORATORY

EUROCORR2018- 9-13 SEPT- KRAKOW

## Major steps of the spent nuclear fuel reprocessing

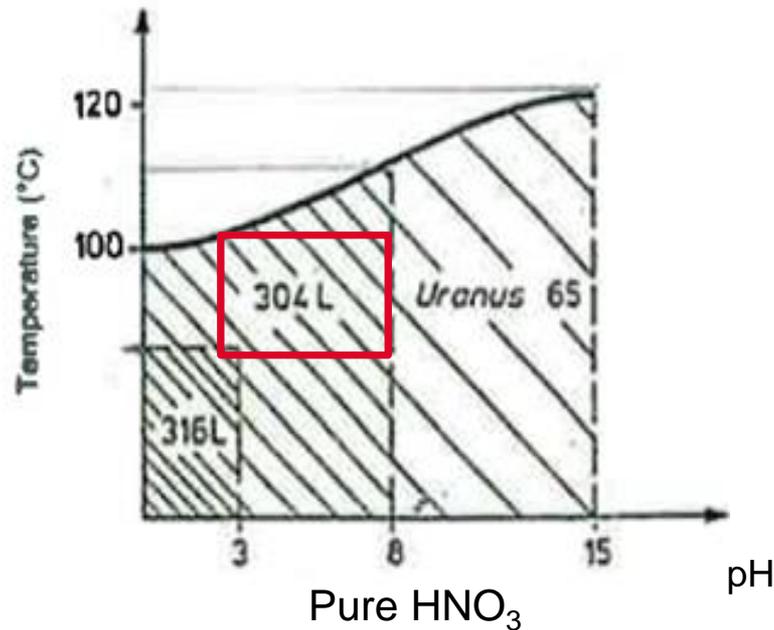
Uranium  
Plutonium  
Minor actinids  
Fission products



Technical Data extracted from orano website

- Prior steps : dissolving and concentrating elements
- Uses high-concentrated and boiling HNO<sub>3</sub> to extract recoverable uranium and plutonium from other fission products.
- But if HNO<sub>3</sub> helps to dissolve fuel, structures are not completely saved...

- Materials selected undergo uniform corrosion in the specific conditions of service. If conditions change (introduction of oxidizing species), corrosion is no more uniform.



Fauvet P., (2012) Corrosion issues in nuclear fuel reprocessing plants, French Energy and Alternative Energies commission (CEA), France.

- For a first approach focus on 304L SS behaviour
- 304LSS probes are easier to supply than other materials

## Current practice

- Corrosion is taken into account by the dimensioning, based on predicting models validated by experimental results.
- Media chemistry is well-known, it is regularly controlled by periodical inspections using non-destructive testings



Require shutdown of the process



Snapshot diagnostic

## Outlook

- For more robustness : collecting real-time data with in-situ ongoing monitoring



Electrical Resistance Probe

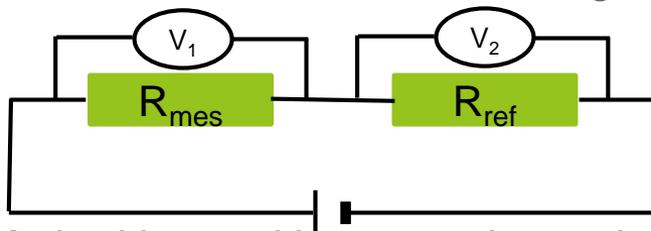
- ER of a straight-lined element is defined by :



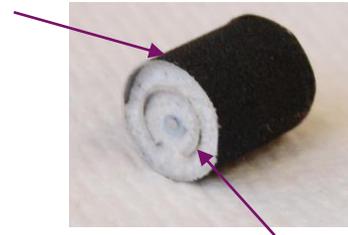
$$R = \frac{\rho \times l}{S}$$

$\rho$  : material resistivity  
 $l$  : length of the element  
 $S$  : cross section area  
 $l$  infinite in regard to  $S$

- Measurement principle: 2 identical resistances (measure and reference) inserted in an electrical circuit. Reference voltage compared to measure voltage.



$$\frac{V_{ref}}{V_{mes}} = \frac{R_{ref}}{R_{mes}} = \frac{th_{mes}}{th_{ref}} = \frac{th_t}{th_{t_0}}$$



- Method is sensitive to section variation
- Customised sensitivity and time of response (depending on corrosion rates expected)
- Independant of media chemistry (unlike other electrochemical methods)
- Resistance value depends **only** on remaining metal thickness



Corrosion rate measurement deduced from change of resistance over a period of time.

- Only reliable in case of uniform dissolution without conductive deposits



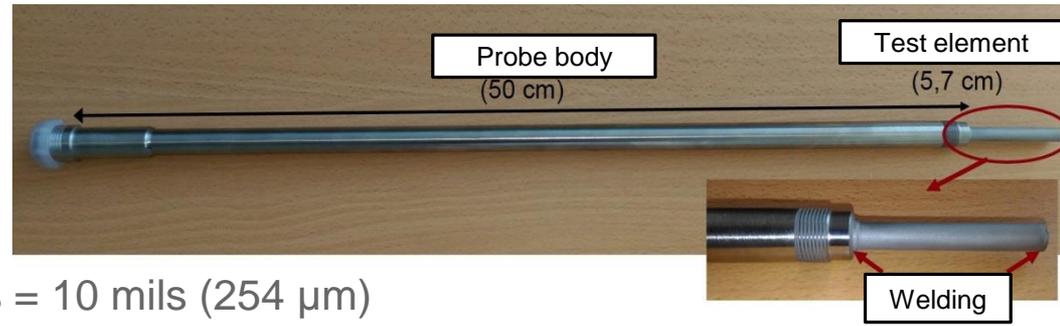
**To study the feasibility of this method in case of IGC model**

- Model 2510 (cylindrical) manufactured by Cosasco®
- 2 tubes identical to test element are supplied for making corrosion coupons



Tile-shaped corrosion coupons

- Tube thickness = 10 mils (254  $\mu\text{m}$ )

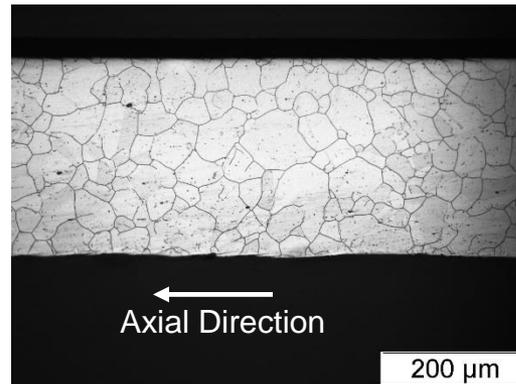
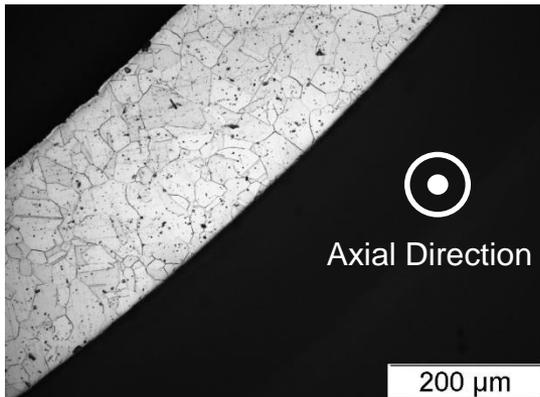


Element	C	Mn	P	S	Si	Cr	Ni	Fe
Content (%w)	0.025	1.89	0.027	0.002	0.31	18.1	9.05	bal.

Chemical analysis of 304L SS (certificate of conformance)

- Microstructure :

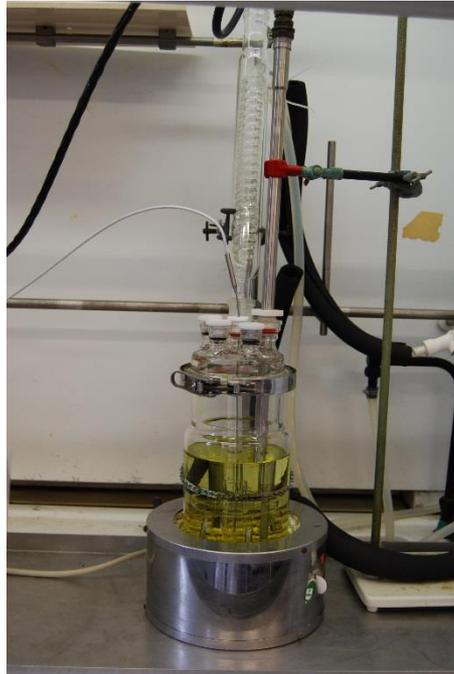
- ❖ mean grain size : 35  $\mu\text{m}$
- ❖ same microstructure in both directions of the tube



- Procedure : comparison of probe's response to gravimetric method
- Test solution : boiling (104 °C) HNO<sub>3</sub> 3 mol/L with 0,8 g/L Vanadium (valency +V)



*Corrosion coupons hung up on a circular sample holder*



**Gravimetric method**  
(reference method)

$$\Delta e = \frac{\Delta m}{S_{\text{sample}} \times \rho}$$

$\rho = \text{volumic weight}$

$\Delta m = \text{weight loss}$

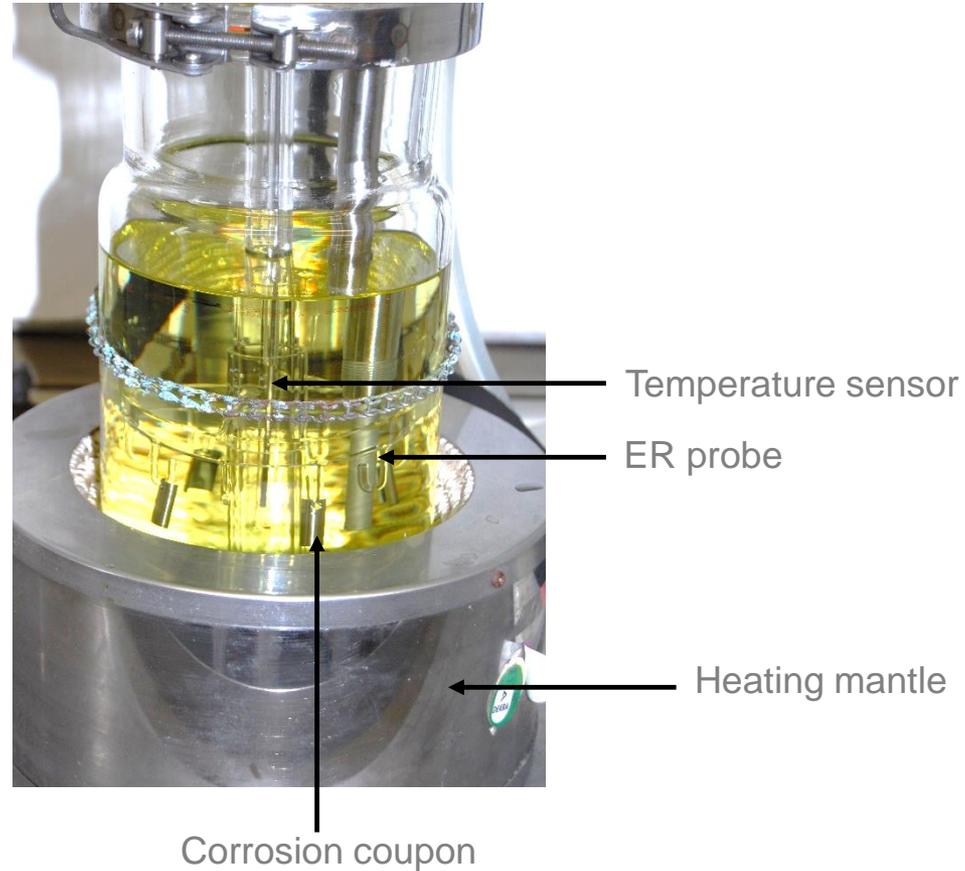
$S = \text{initial surface of the sample}$

## EXPERIMENTAL SETUP

- Procedure : comparison of probe's response in InterGranular Corrosion mode to gravimetric method
- Test solution : boiling (104 °C)  $\text{HNO}_3$  3 mol/L with 0,8 g/L Vanadium (valency +V)



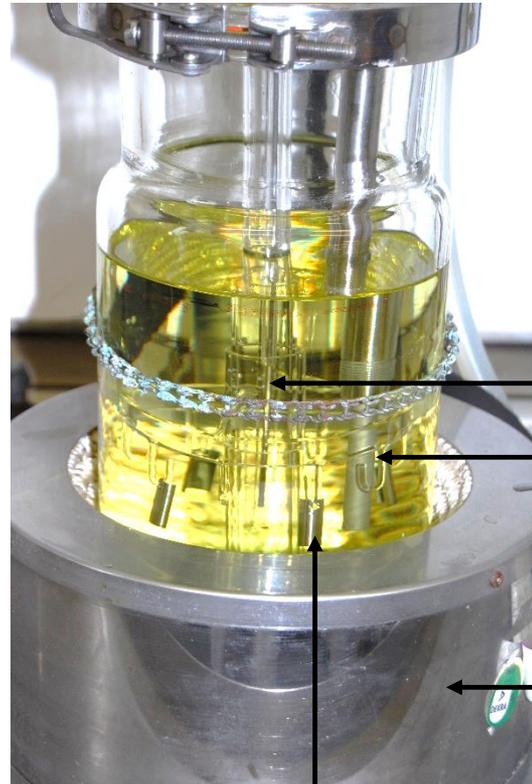
*4 corrosion coupons hung up on a circular sample holder*



- Procedure : comparison of probe's response in InterGranular Corrosion mode to gravimetric method
- Test solution : boiling (104 °C)  $\text{HNO}_3$  3 mol/L with 0,8 g/L Vanadium (valency +V)



*4 corrosion coupons hung up on a circular sample holder*



Temperature sensor

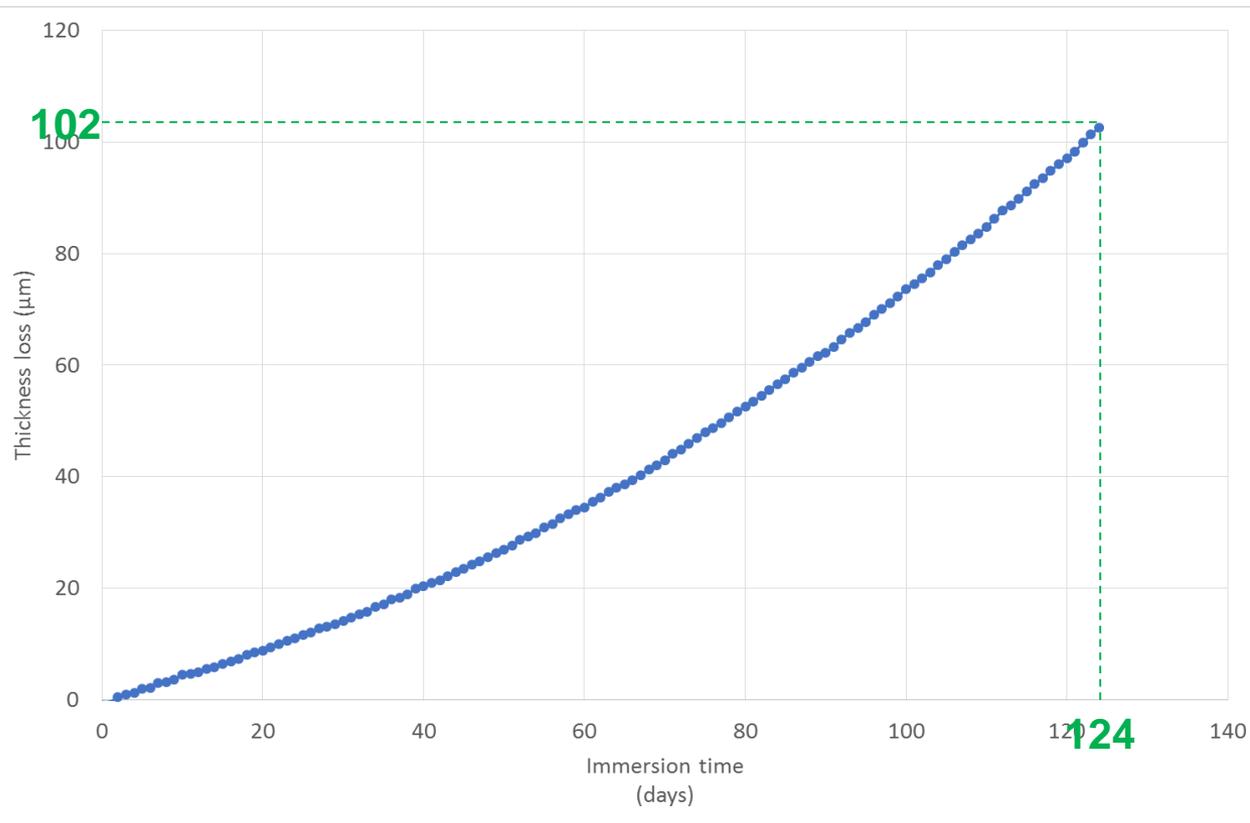
ER probe

Heating mantle

Corrosion coupon

- Coupons are withdrawn after 308 h, 633 h, 982 h and 1532 h of exposure time.
- Probe acquiring frequency is 2 h.

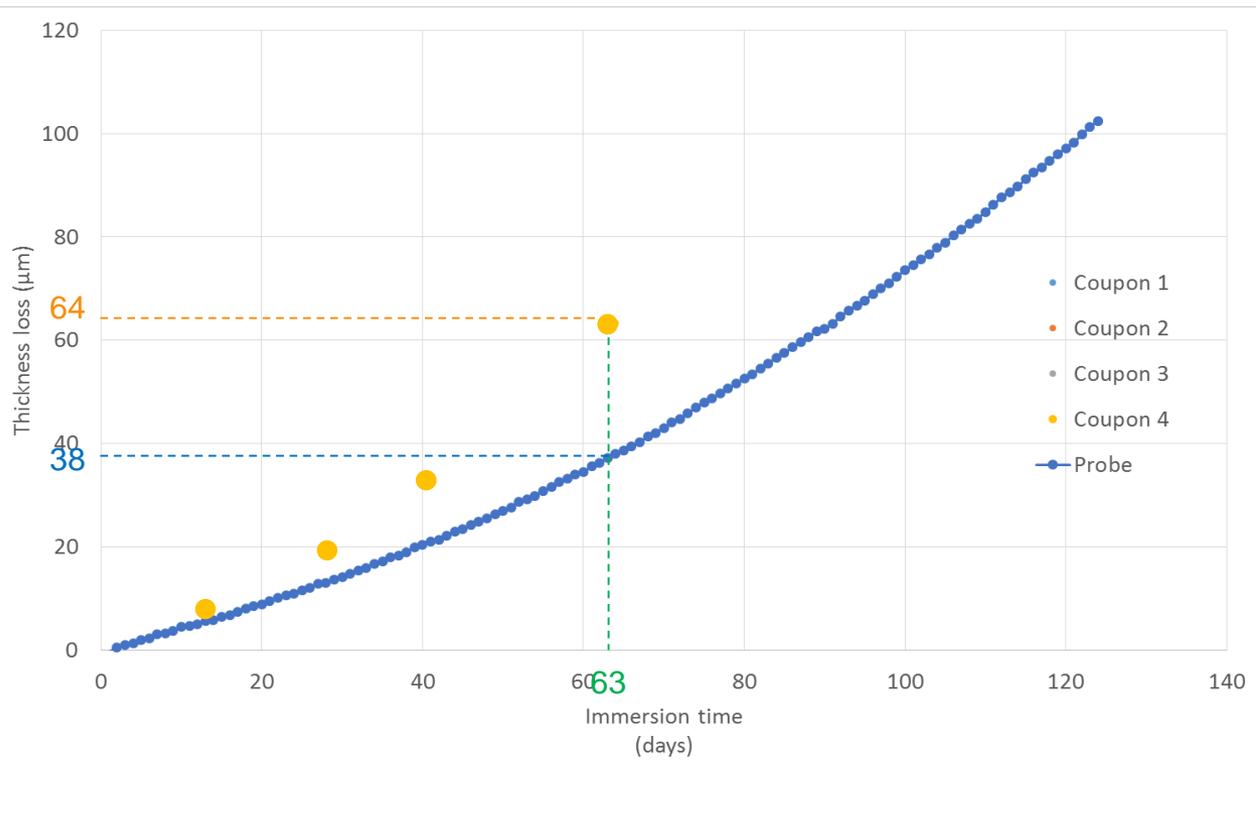
### Evolution of thickness loss read by ER probe



- Test is stopped before span is reached (125 µm)
- Solution is not renewed during the whole test
  
- **Non-linear evolution with time**
- **Global thickness loss after 124 days = 102 µm, Global apparent corrosion rate : 300 µm/year**

# ER PROBE RESULTS COMPARED TO CORROSION COUPONS

Evolution of thickness loss determined by ER probe and by coupons mass loss vs time



- Values for coupons are repeatable
- They differ from probe's values
- The gap increase with time
- Probe seems to minimize thickness loss

- After 63 days thickness losses (µm) :

<i>Probe</i>	<i>Coupons</i>
38	64

- After 63 days apparent global  $r_{\text{corr}}$  (µm/year):

<i>Probe</i>	<i>Coupons</i>
220	360

- Global apparent  $r_{\text{corr}}$  increase with time in both cases → corrosion is not uniform.
- These rates are comparative parameters but what is their meaning?

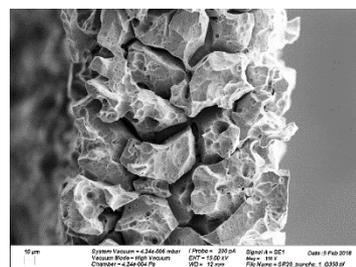
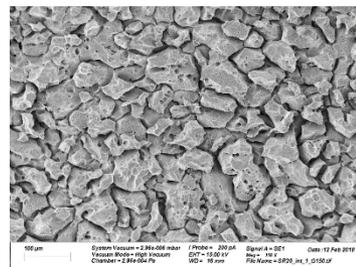
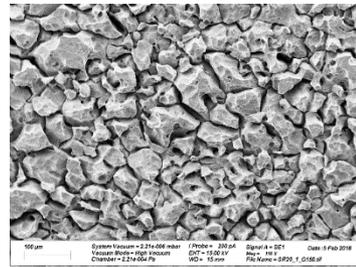
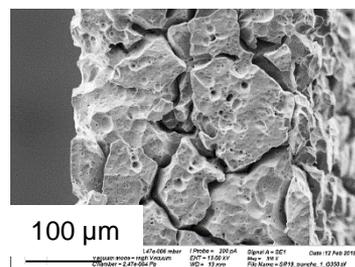
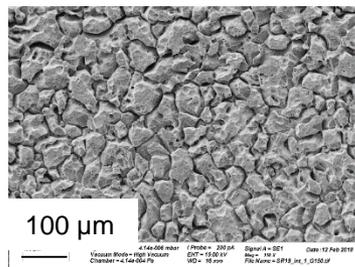
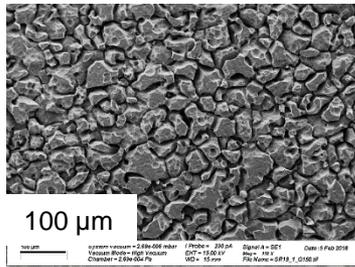
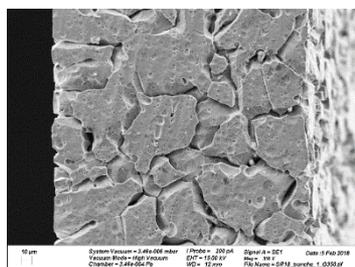
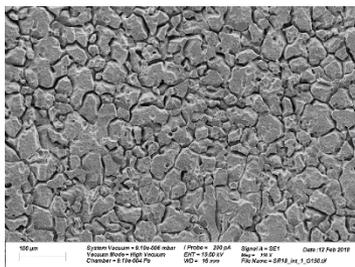
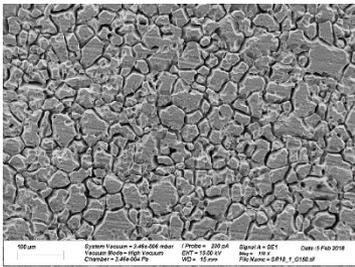
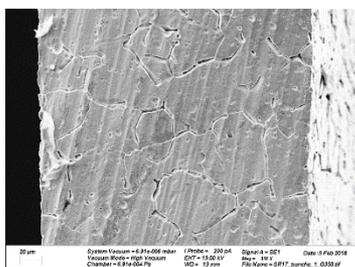
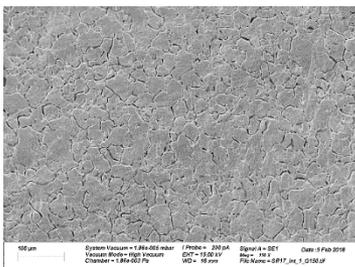
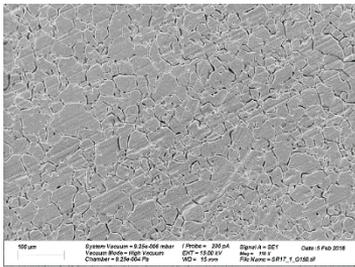
# COUPONS SURFACE EXAMINATION

308 h

633 h

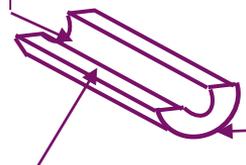
982 h

1532 h



Concave surface

Convex surface



Cross section of the tiles (longitudinal direction)

Grains marking

Grains engraving

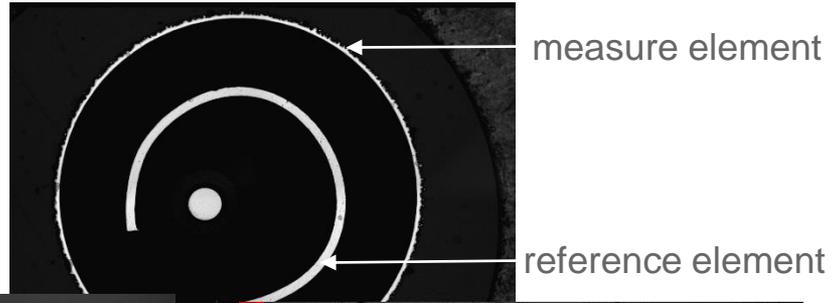
deeper groves

grains dropping  
*(no remains of ancient surface)*

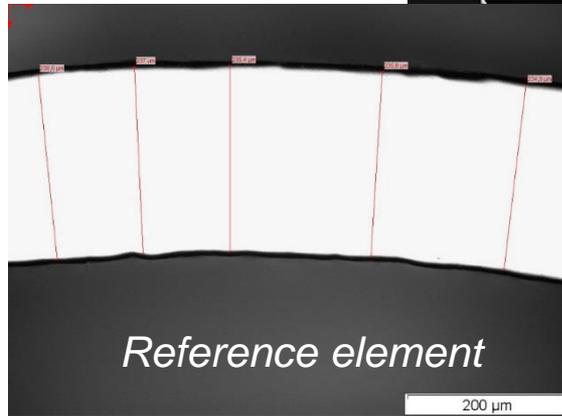
# PROBE CROSS SECTION EXAMINATION

■ End of test (after 124 days of immersion)

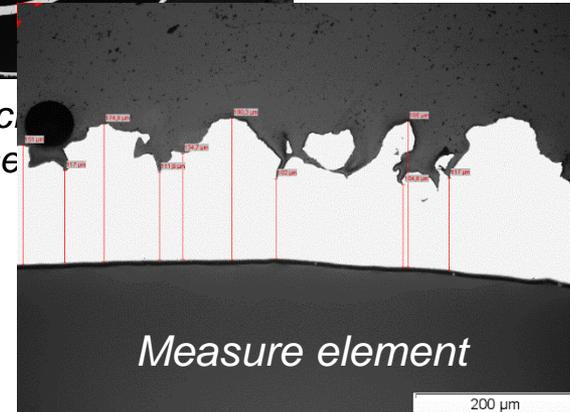
*Section of the probe element with cement inside and inner concentric reference element*



Section micrographs



ed c  
the



■ Mean values of residual (probe element) and reference thickness (μm)

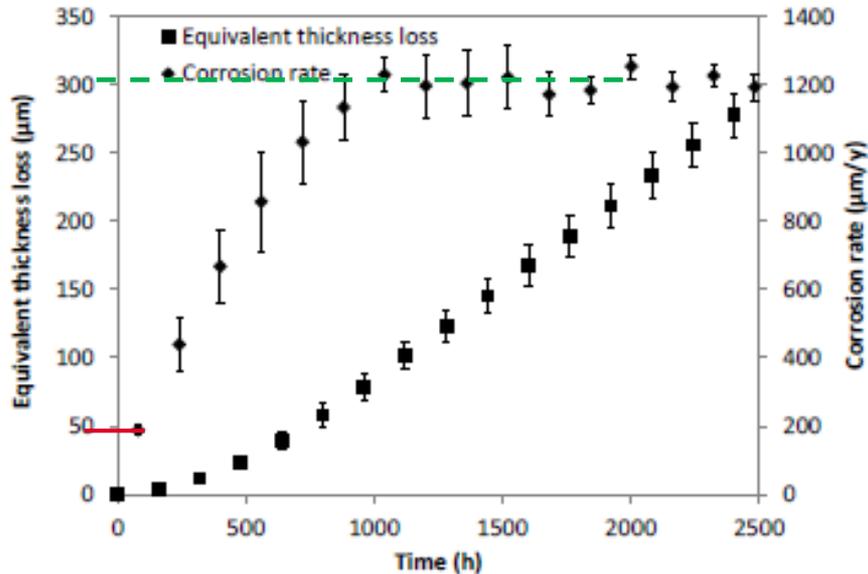
Tops	Bottoms	Mean value	Reference tube
163 ± 18	114 ± 16	136 ± 29	240 ± 8

■ Deduced dissolved thickness :  $th_{cor=}$  104 μm ➔ consistent with probe value (102 μm)

■ ER probe returns « mean » results consistent with observations, even if this « mean » corroded thickness is not relevant because it doesn't reflect the thinnest value.

## MECHANISM FOR IGC MODE

- **Statement** : evolution of thickness loss follows a trend, and also its derivative:

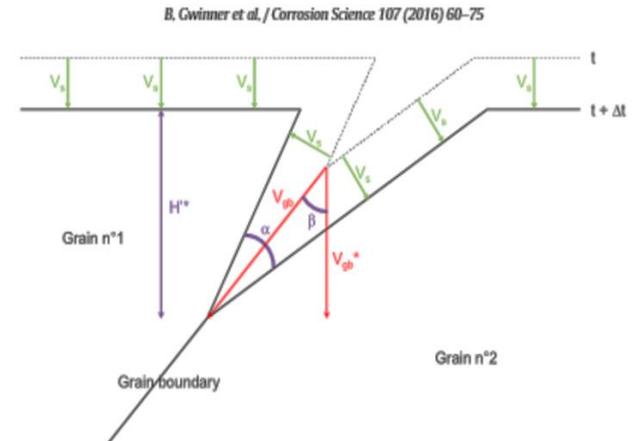
Mechanism proposed to explain this trend :

- At the beginning, only surfaces dissolve.
- Corrosion rate increases linearly until a steady-state value;
- This value corresponds to 1st grain's raw dropping and dropping becomes predominant

- IGC results from difference between corrosion kinetics of **grain surface** and **grain boundaries**.

$V_S$  : corrosion rate of grain surface

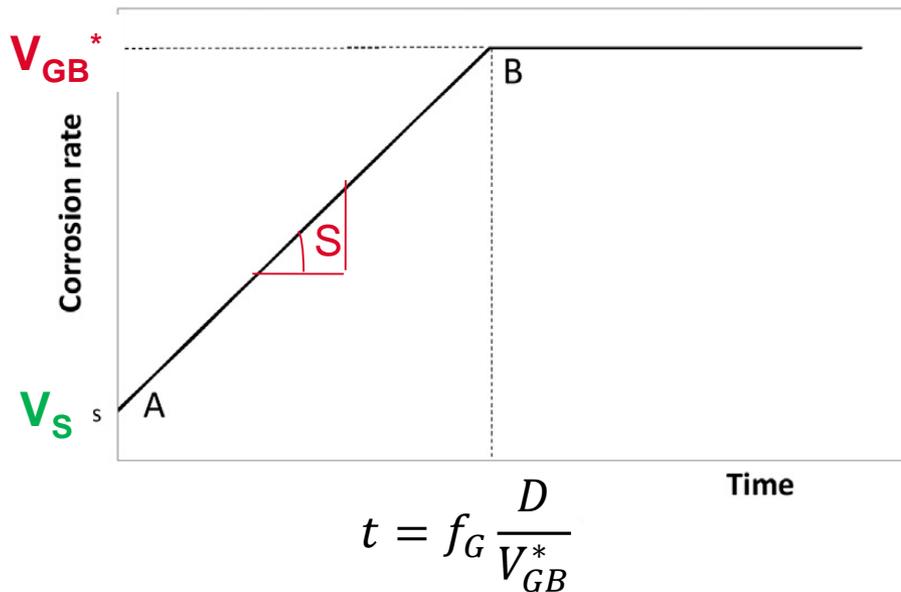
$V_{GB}$  : corrosion rate of grain boundary  $\longrightarrow V_{GB}^*$



- **SCIANS** : « laboratory-made » tool developed to simulate IGC in steels based on the shape of the mass loss kinetics. (B. Gwinner and Al / Corrosion Science 107 (2016)/60-75)

### SCIANS Assumptions :

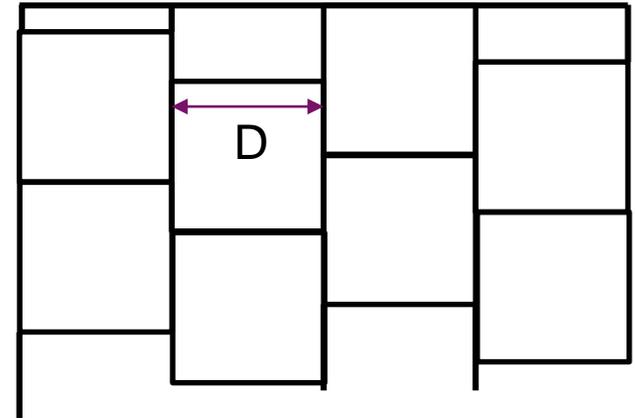
- ❖  $V_S$  and  $V_{GB}^*$  are identical and constant in time all over the surface
- ❖ Grains geometry is simplified (square grains)



- The initial value corresponds to  $V_S$  (initial dissolution of metal)
- Stationary value corresponds to 1st grains row's dropping and is equal to  $V_{GB}^*$ .
- The transition time is linked to grain size  $D$  and  $V_{GB}^*$  and a geometrical factor  $f_G$ .

- SCIANS analytical model enables to calculate  $V_{GB}^*$  :

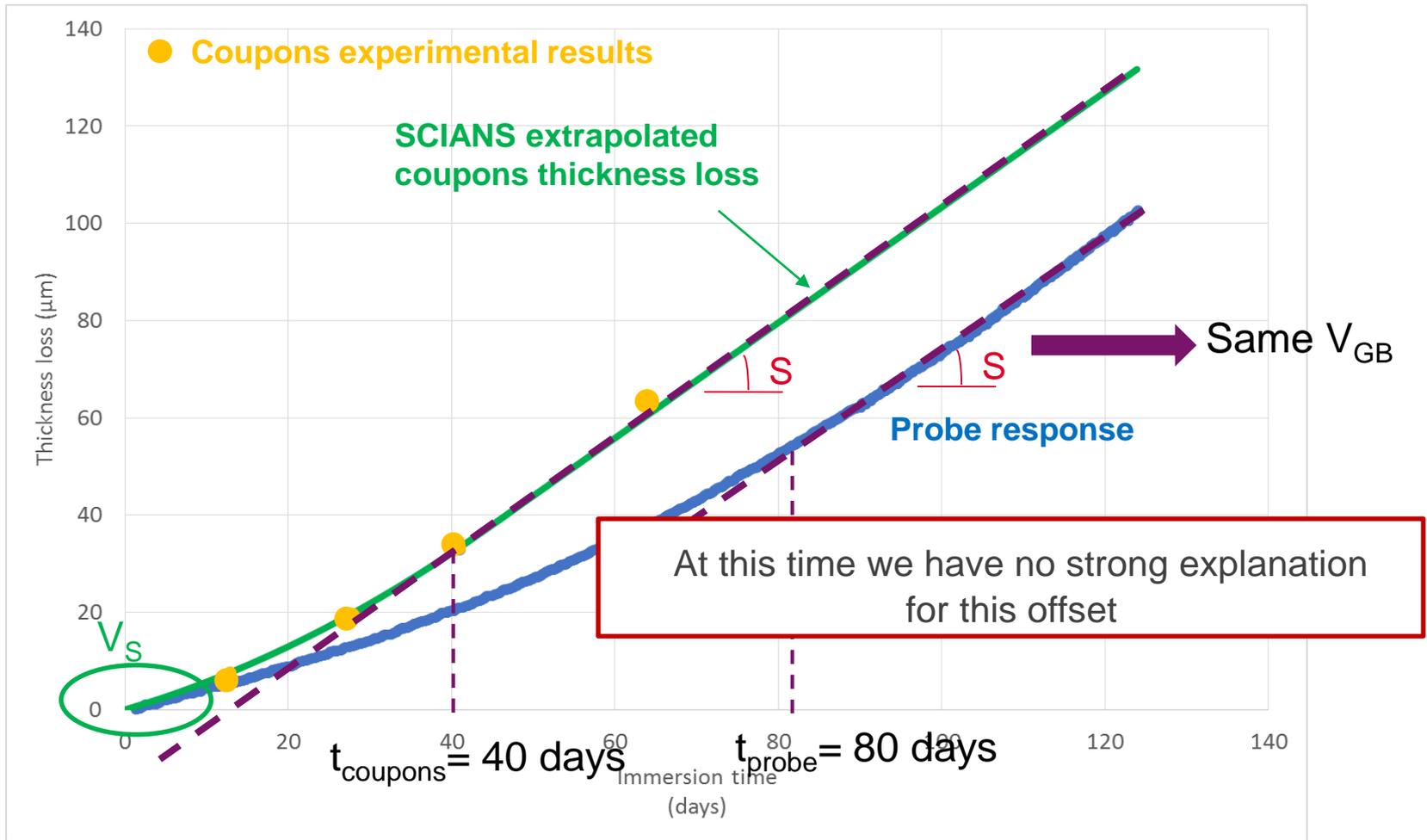
$$V_{GB}^* = \frac{V_S}{2} + \sqrt{\left(\frac{V_S}{2}\right)^2 + \frac{3}{2} \times slope \times D}$$



Schematic illustration for the determination of the transition time

$V_S$  is the y intercept ,  $D$  is a material data (measured) and slope is deduced from experimental date.

# Extrapolation of coupons thickness loss using SCIANS compared to probe response



Same  $V_S = 180 \mu\text{m}/\text{year}$

Same  $V_{GB}^* = 430 \mu\text{m}/\text{year}$

Transition times are different (twice as the coupons for the probe): due to a different geometrical factor  $t = f_G \frac{D}{V_{GB}^*}$

- In this very corrosive media, ER probe resisted and gave a response during 3 months
- Thickness loss measured by ER probe is lower than that measured by gravimetric method at the same time
- Corroded thickness measured by the probe is relevant with mean remaining thickness observed on polished cross-section
- Apparent corrosion rate has no sense ;  $V_{GB}^*$  is the most important parameter
- Using IGC simulating model SCIANS, it becomes possible to infer  $V_{GB}^*$  .
  - Outlook in-service applications.
- *Currently, no reliable explanation of the offset between gravimetric and ER probe....but it is under investigation*
  - *size effect (surface probe is 5 times more important)?*
  - *effect of geometry (edges or tips)?*
  - *current effect?*

**Thanks for your attention**

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