# INVESTIGATION OF SINGLE PIT PROPAGATION ON 316L STAINLESS STEEL

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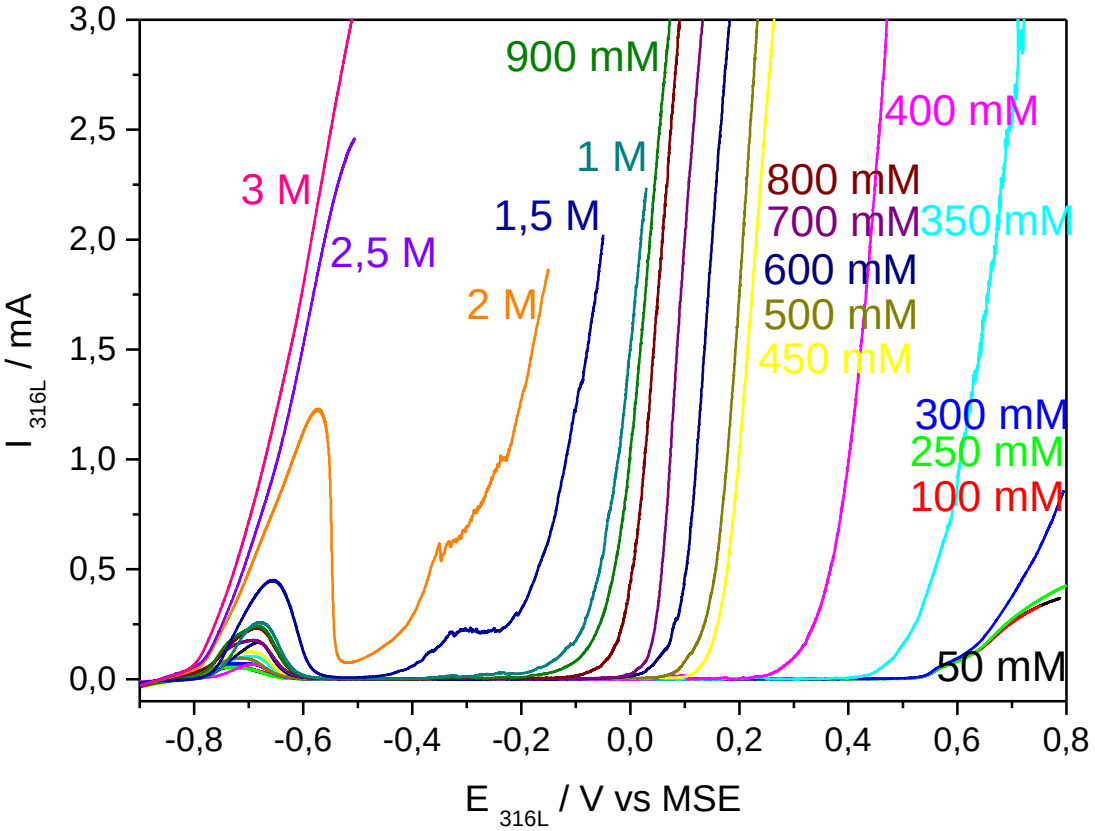
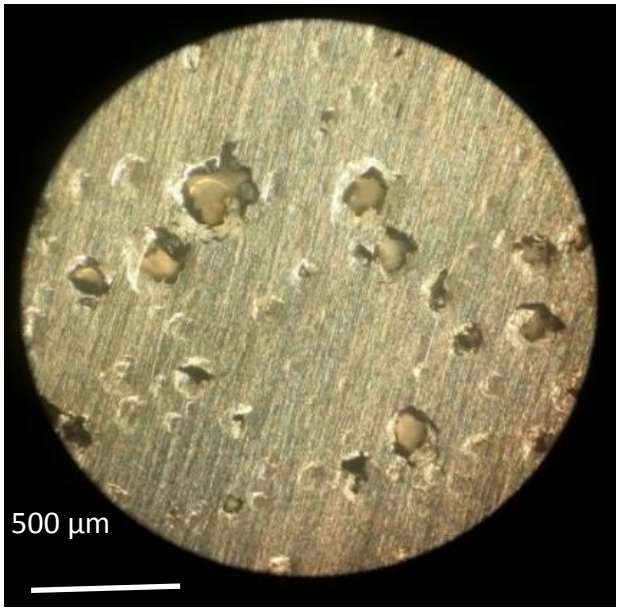
# Introduction



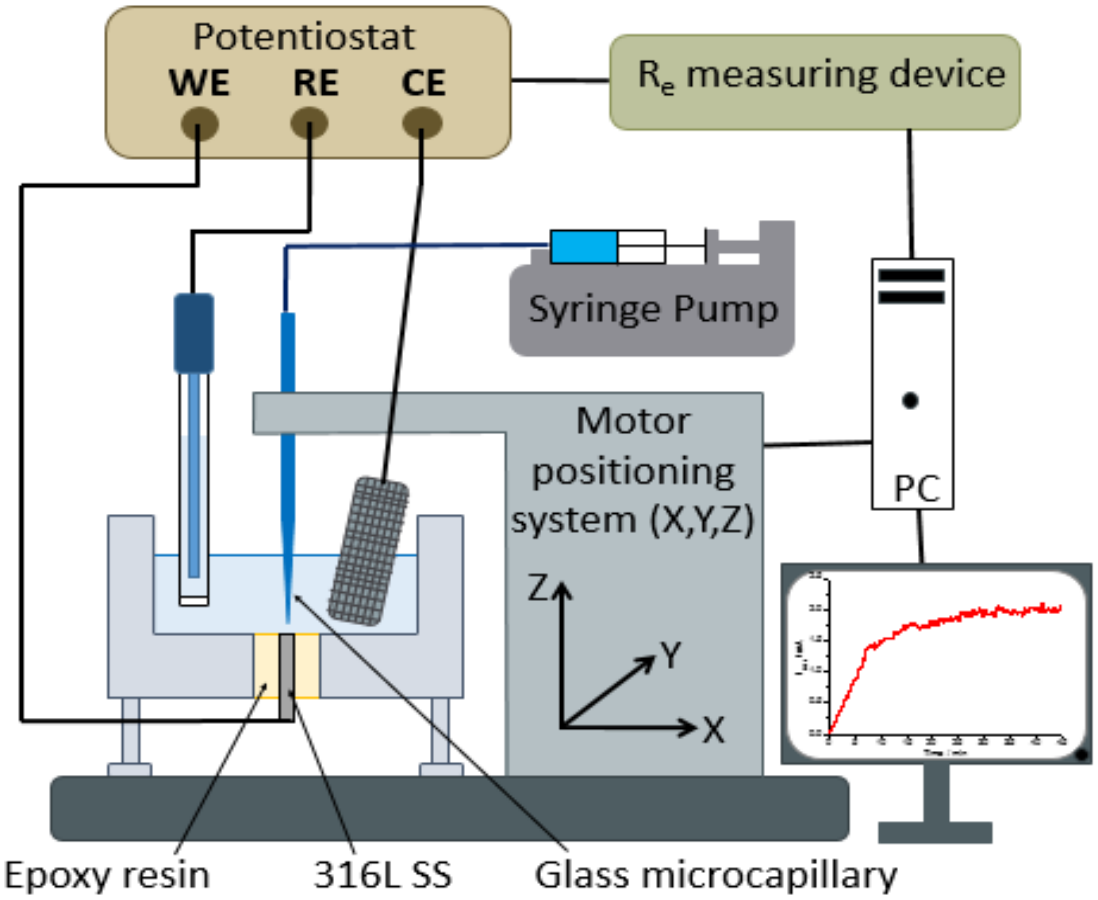

*Influence of the NaCl bulk concentration on the pitting potential*
*Scan rate: 1 mV/s*



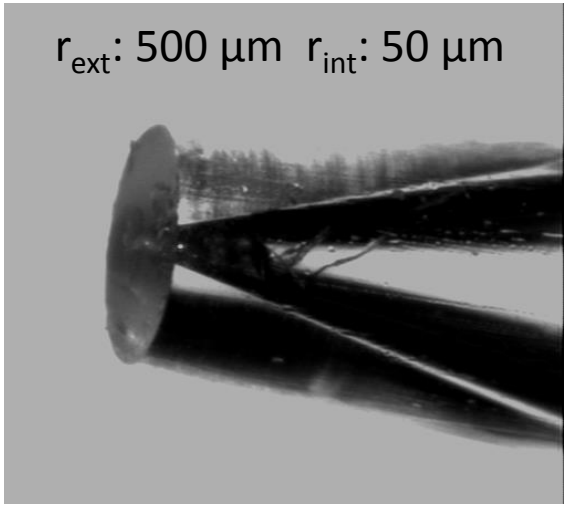

*Optical image of several pits for 316L stainless steel in 0.5 M $H_2SO_4$ + 0.6 M NaCl*

Pitting corrosion for 316L stainless steel in a chloride environment is stochastic

# Experimental setup to generate a single pit




*Flow microcell used to generate a single pit*




*Use of a glass microcapillary for controlling the amount of chloride ions in a 0.5 $H_2SO_4$ solution*

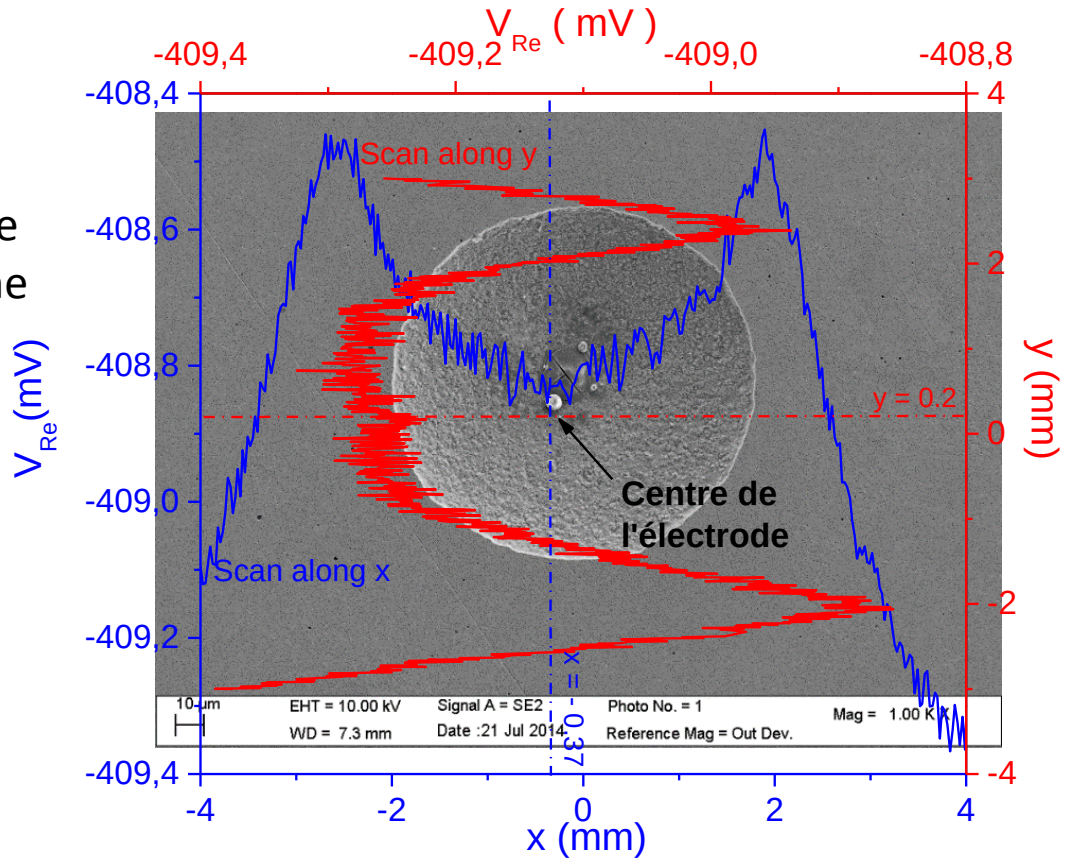
# Experimental setup to generate a single pit

**Microcapillary positioning**

Measurement of the electrolyte resistance variation due to the presence of the capillary in the close vicinity of the stainless steel electrode

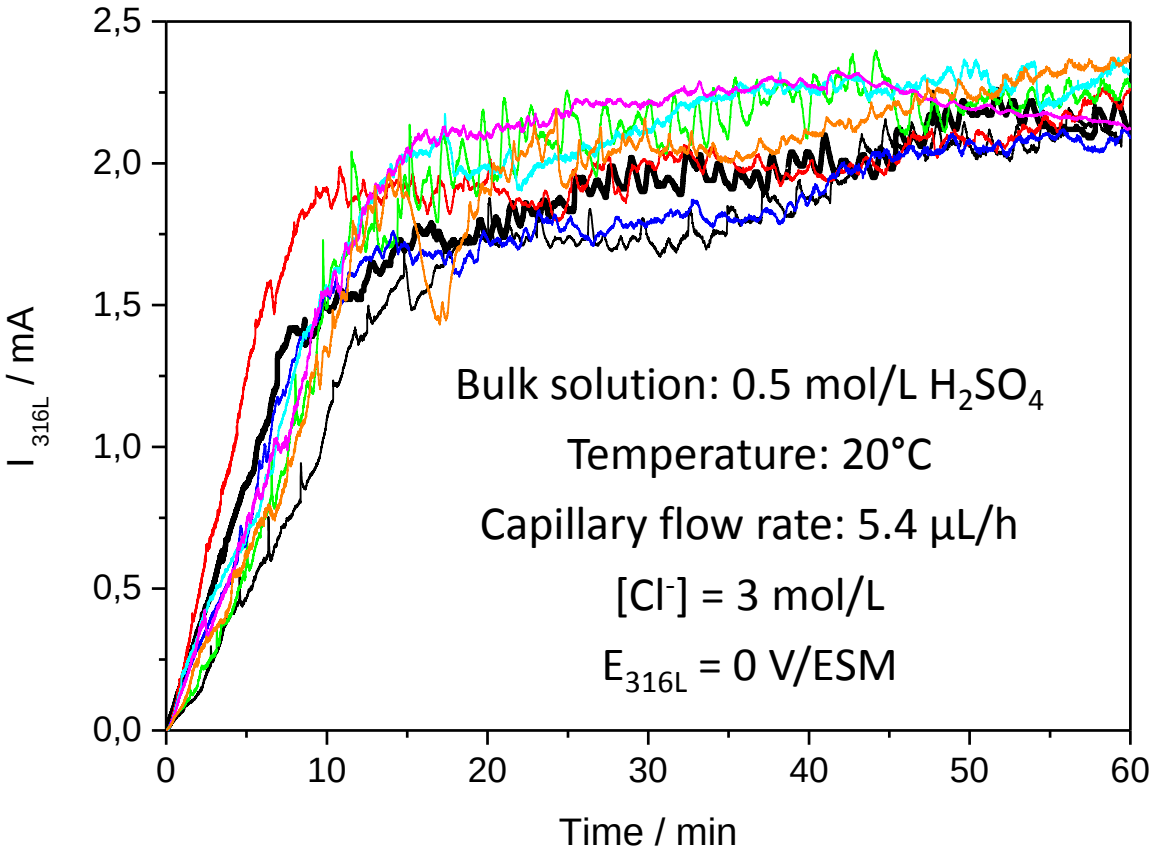
**Single pit initiation**

Release of chloride ions with the microcapillary in a sulfate bulk

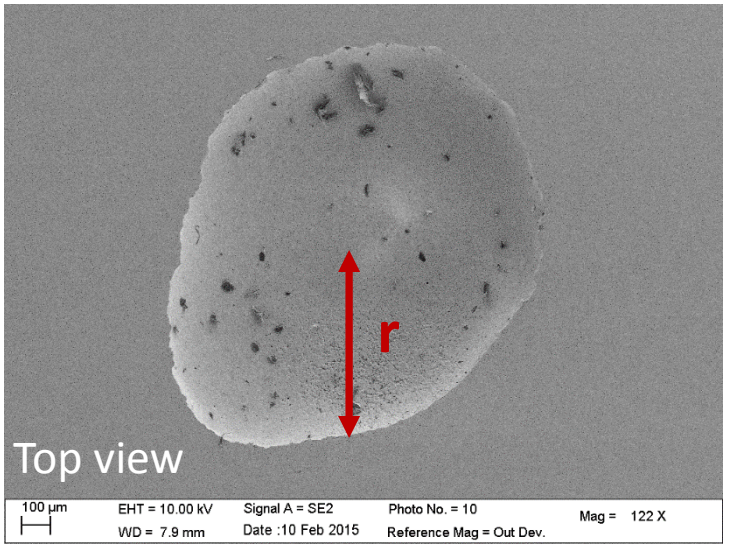


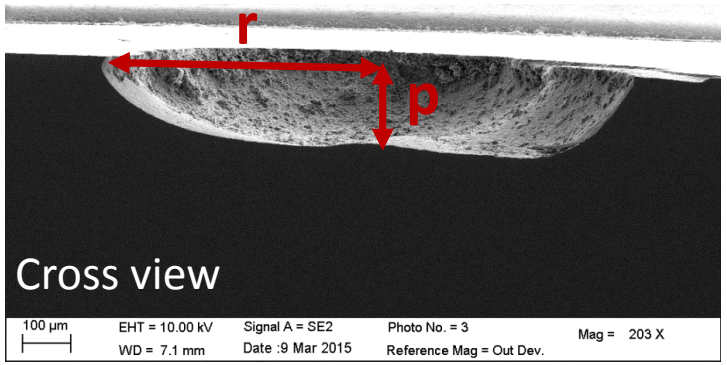
# Reproducibility and characterization

Example of 7 identical experiments




Disk-shaped pit characterized by a pit radius and a pit depth




*SEM observations for a single pit after 1 h of propagation*

# Empirical laws

From microscopy measurements

- For t > 180 s: pit radius

$$r(\mu m) = 250 + 26.36 * |t(s) - 180|^{0,34}$$

- For t > 2700 s: pit depth

$$p(\mu m) = 126 + 1.57 * |t(s) - 2700|^{0.54}$$

**The depth increases with $\sqrt{t}$**

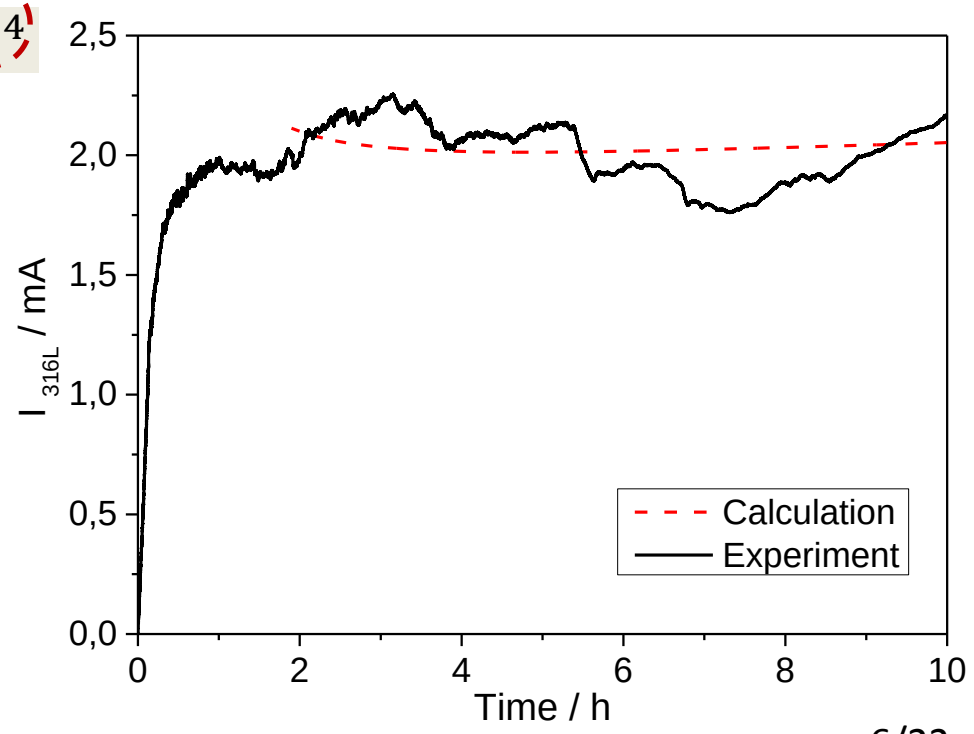
→ 2 possible limiting mechanisms:

- Diffusion
- Ohmic control

Comparison with the pitting current

Pit volume $V_{pit} = \pi * r^2 * p$

Faraday's law $I = \frac{\rho n F}{M} \frac{dV}{dt}$

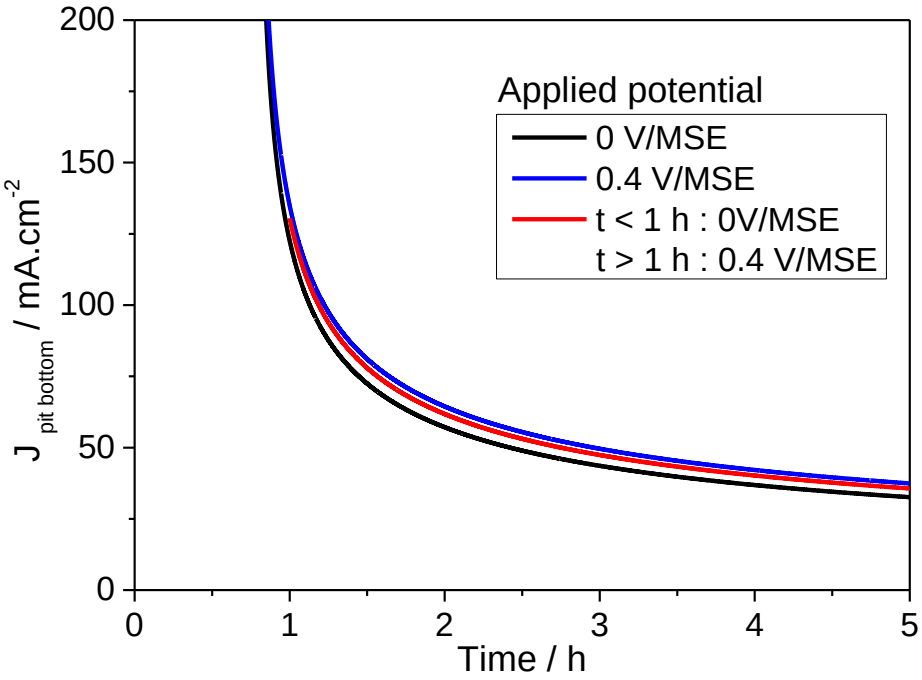


# Determination of local limiting mechanisms

Parameters: 0.5 M $H_2SO_4$ – [$Cl^-$] = 3 M – flow rate = 5.4 µL/h – 20 °C

Experiments carried out at **different applied potentials**

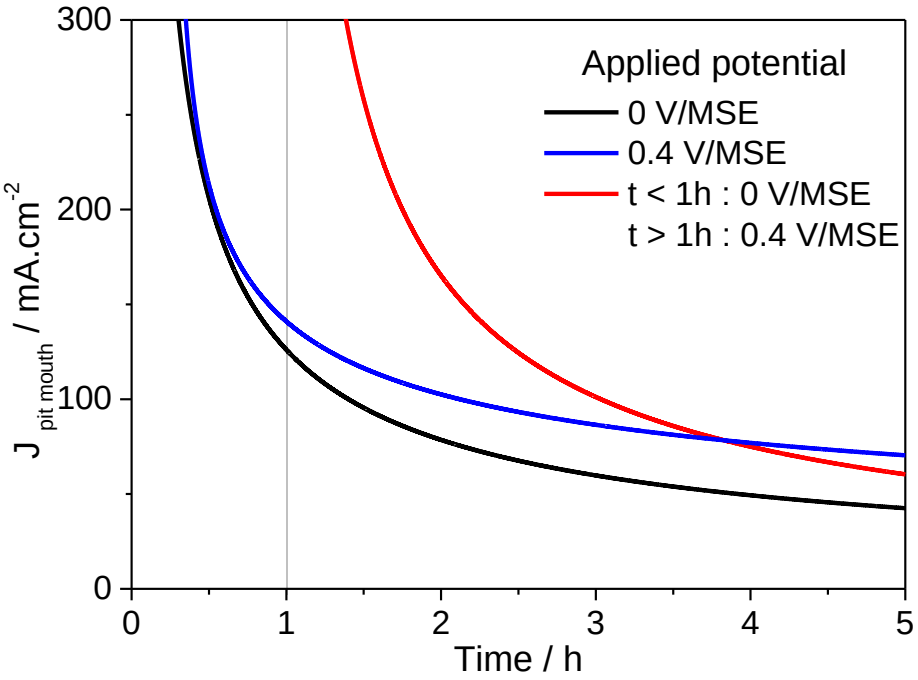
## *Pit bottom*




Pit bottom current density not affected by the potential

→ **Diffusion controlled mechanism**

## *Pit mouth*

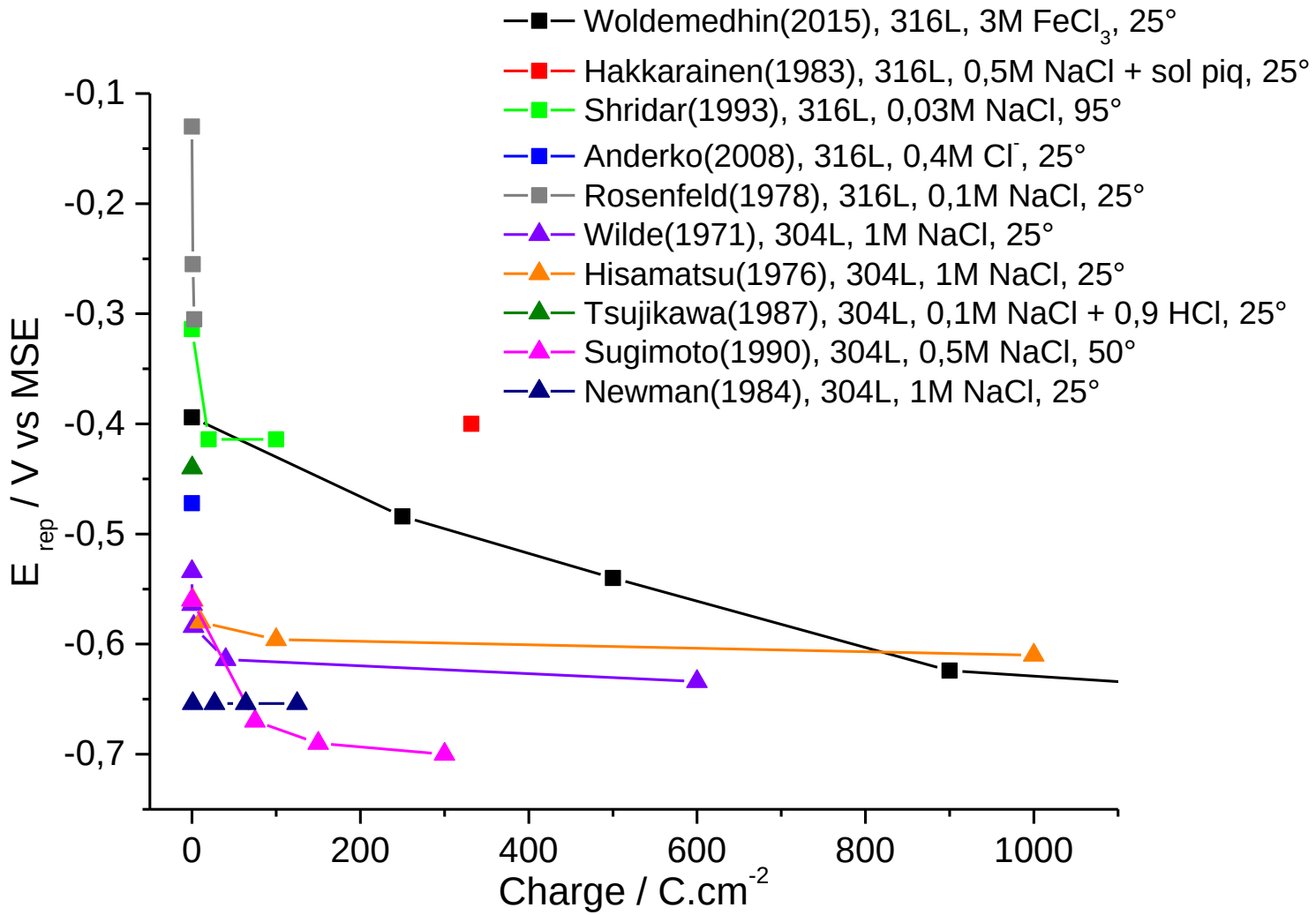



Pit mouth current density affected by the potential

→ **Potential control of the pit mouth**

More details in S. Heurtault, *Electrochimica Acta* (2015) in press

# How to characterize the pit repassivation ?

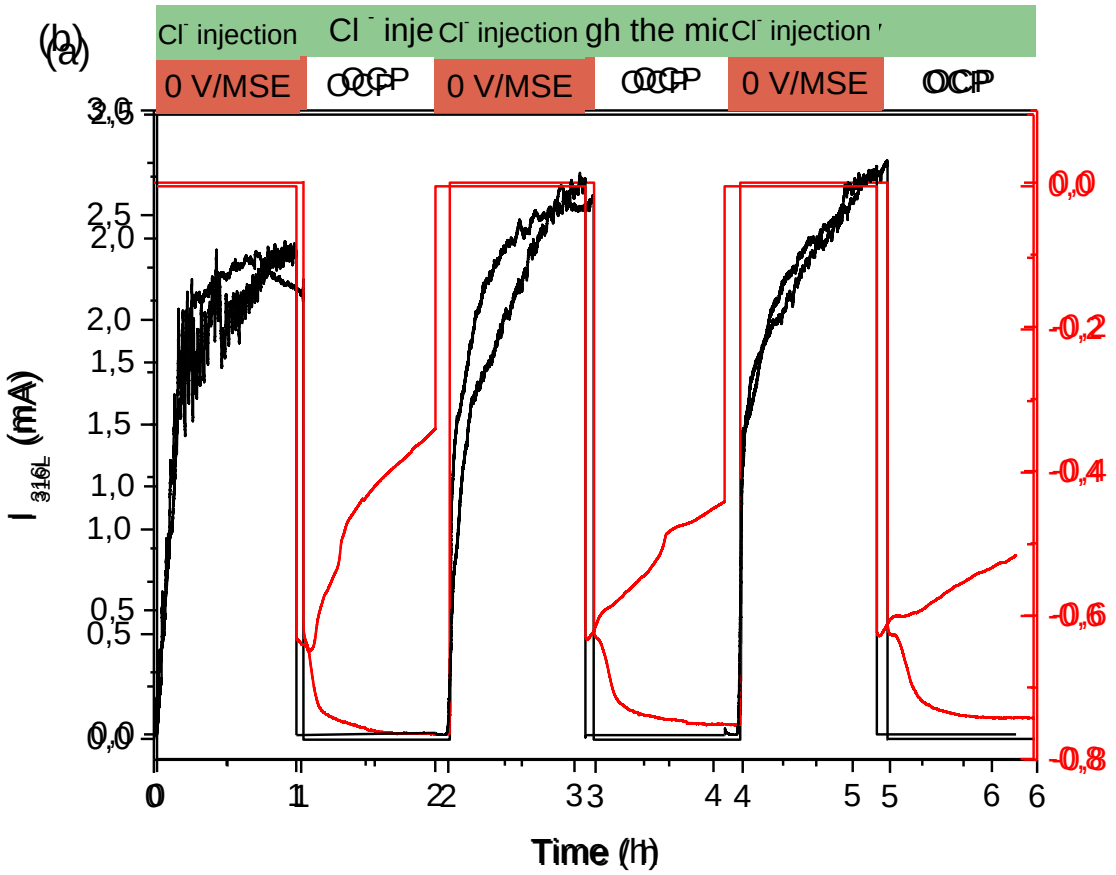


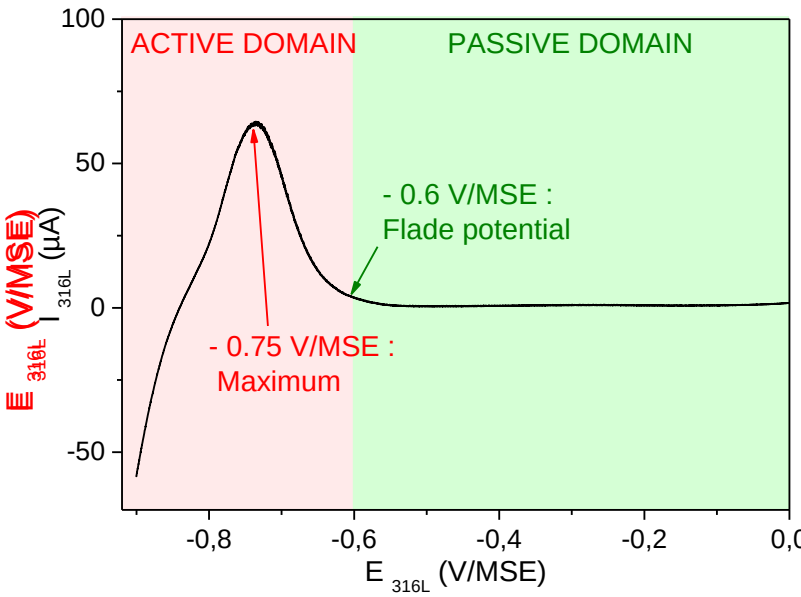

*Repassivation potentials for 304L (triangle) or 316L (square) stainless steel in chloride bulk*

The repassivation potential measurements can determine the pit repassivation.
Easiest repassivation for 316L than for 304L stainless steel

# Role of chloride ions in pitting corrosion

Experiments performed in 0.5 M $H_2SO_4$ at 20°C with [$Cl^-$] = 3 M (flow rate: 5.4 µL/h) and alternating OCP and polarization at 0 V/MSE



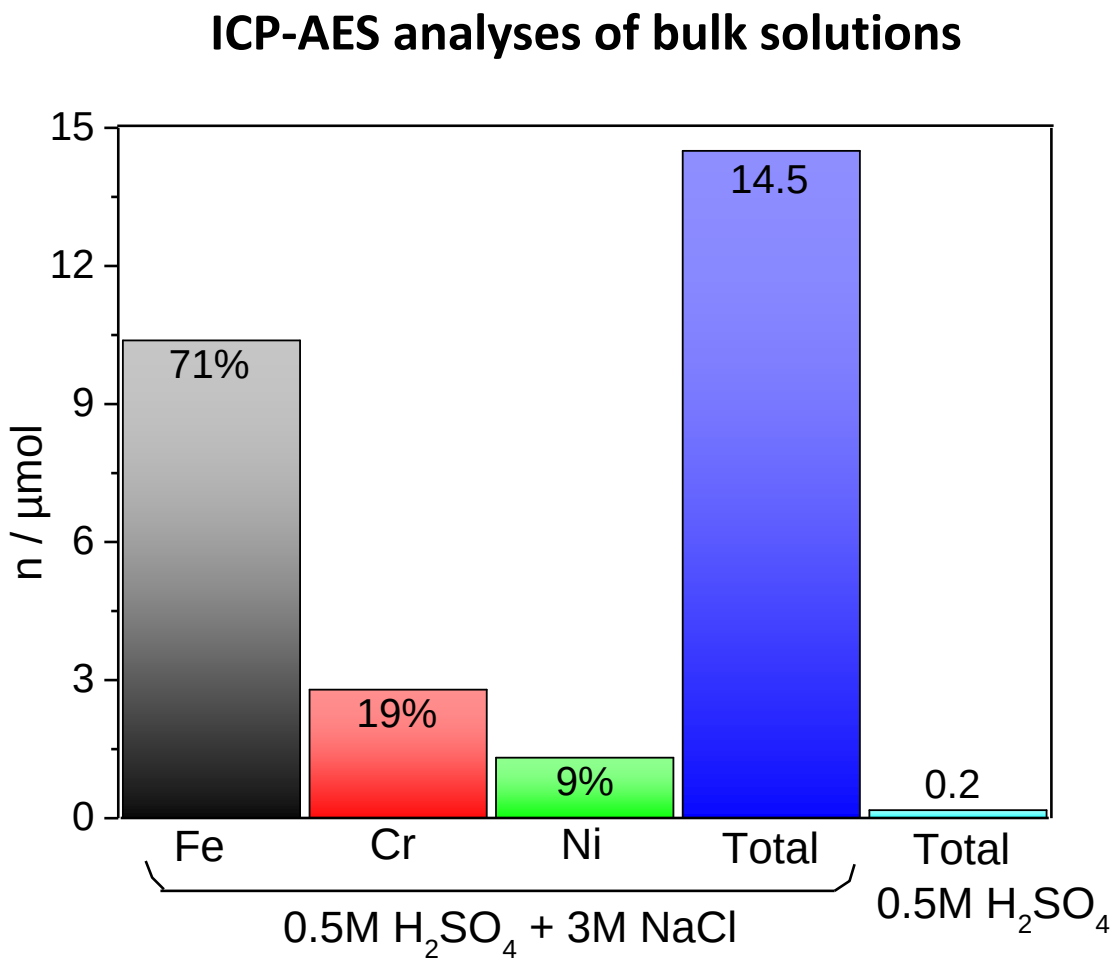




If the $Cl^-$ supply is stopped, the OCP goes back to the passive domain

If the $Cl^-$ supply is maintained, the OCP remains in the active domain

# ICP analyses of 316L SS dissolution with and without 3M NaCl

316L SS was dissolved at OCP during 15 hours in 0.5M $H_2SO_4$ and 0.5M $H_2SO_4$ + 3M NaCl

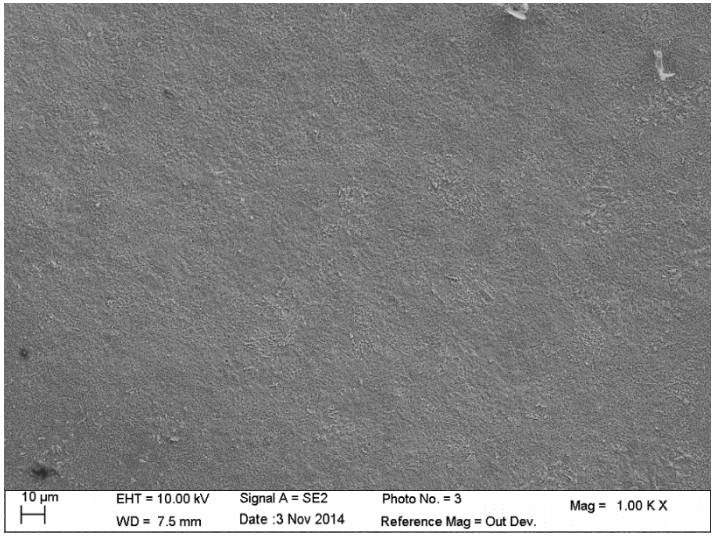



ICP analyses confirm that 3M NaCl increases the corrosion rate

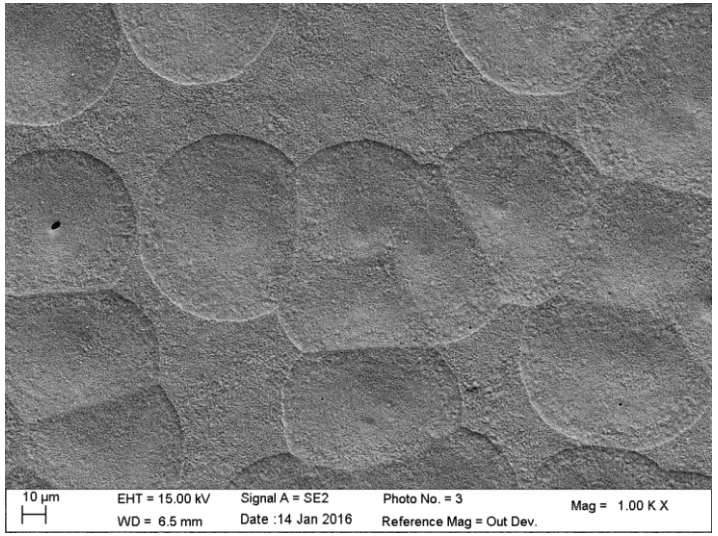
# How evolves the pit during the OCP phases ?

**Microscopy measurements**: no evident evolution of pit depth and pit radius.

**Pit bottom morphology:** localized attacks in presence of $Cl^-$




*Pit bottom after OCP without $Cl^-$*




*Pit bottom after OCP in presence of $Cl^-$*

Slight propagation at the OCP when the $Cl^-$ supply is maintained

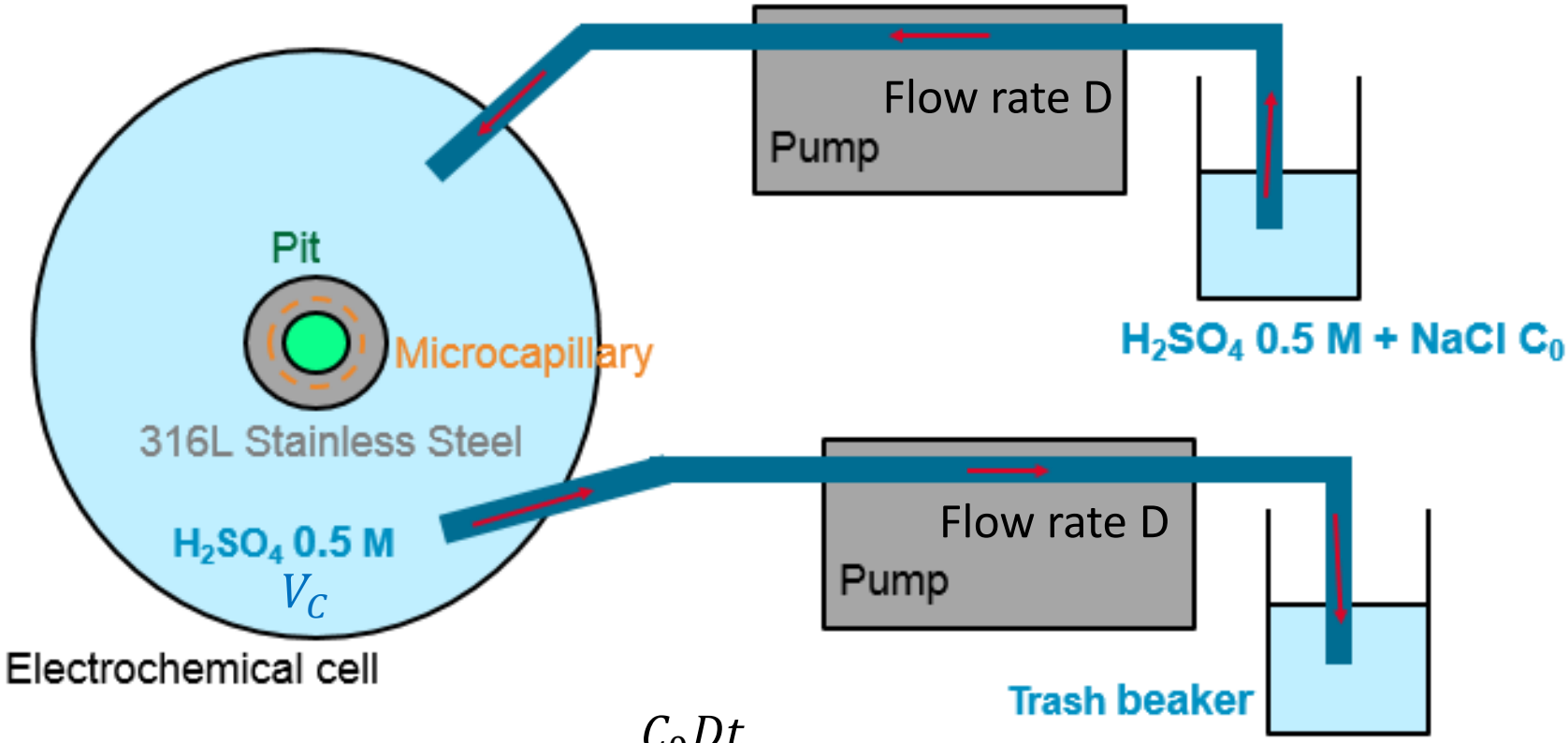
OCP recorded after a propagation + ICP analyzes + SEM images

→ **Important role of $Cl^-$ ions in pitting corrosion**

# Use of peristaltic pumps to change the solution

**Experimental procedure**

1. Initiation of a single pit under the microcapillary
2. Use of peristaltic pumps to change the solution from 0.5 M $H_2SO_4$ to 0.5 M $H_2SO_4$ + $C_1$ NaCl
3. Removal of the glass microcapillary

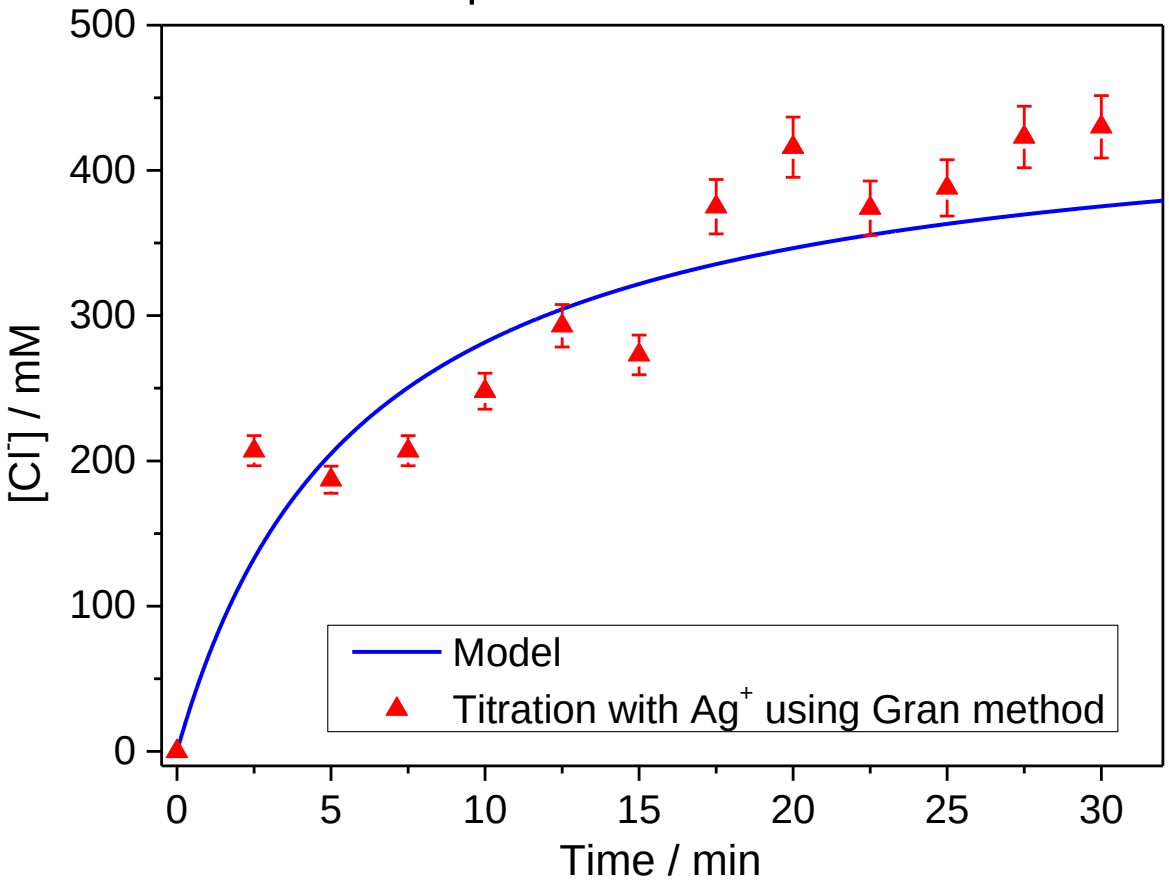



$$New\ [Cl^-]\ in\ the\ cell: C_1 = \frac{C_0 Dt}{V_C + Dt}$$

# Verification of bulk chloride concentration

$$C_0 = 450\ mM\ NaCl\ ;\ V_C = 40\ mL\ ;\ D = 7\ mL/min$$

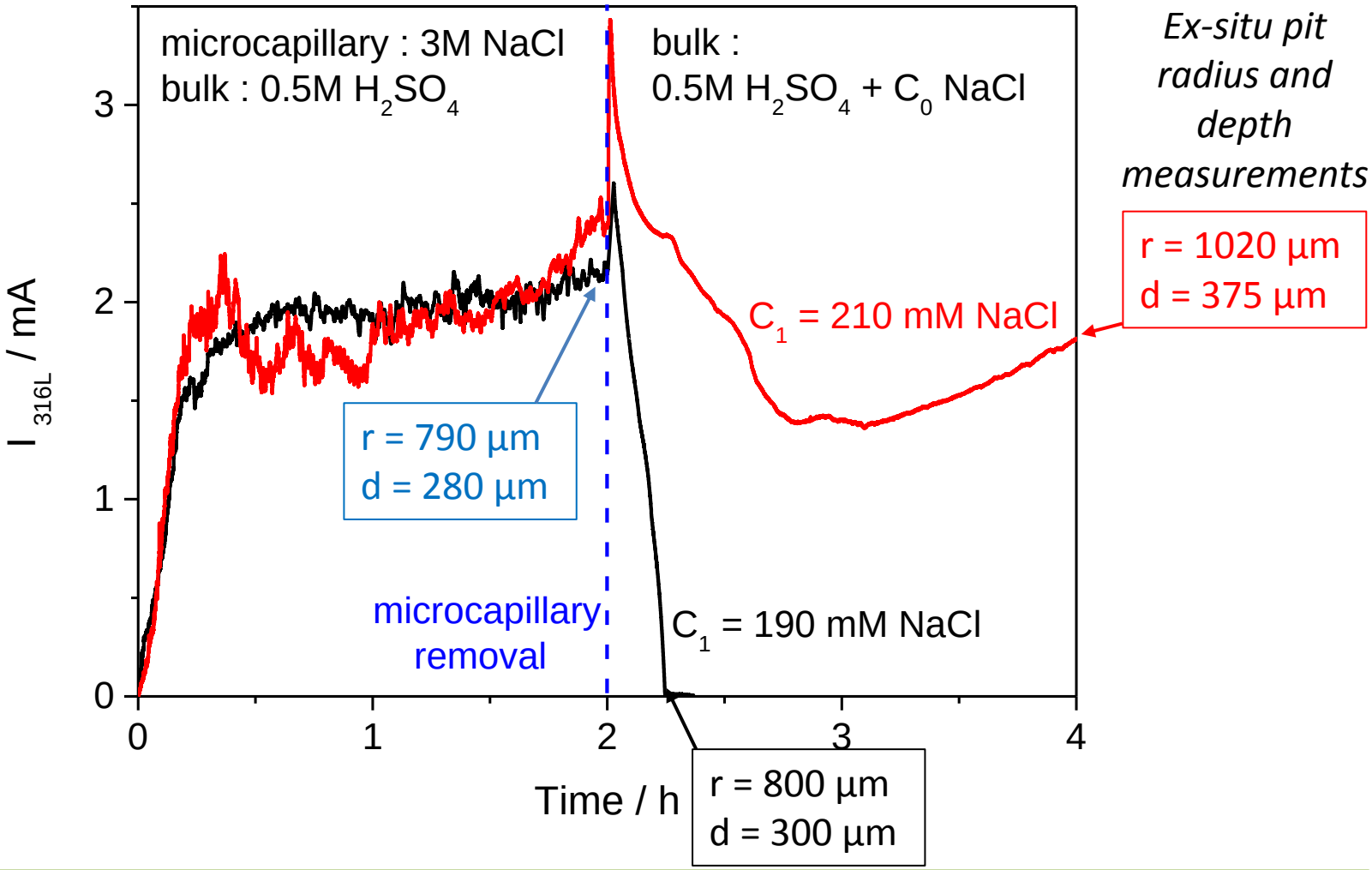
Comparison of the model with experimental results for which $Cl^-$ titration has been performed each 2.5 min




Good prediction of the bulk chloride concentration after the use of peristaltic pumps
Measurement error: less than 5%

# Determination of the repassivation $Cl^-$ concentration

**Repassivation concentration**: minimum chloride concentration necessary in the bulk for sustaining the pit propagation




At 0 V/MSE and T = 20°: **190 mM NaCl < $C_{repassivation}$ (2 hours) < 250 mM NaCl**

# Reproducible repassivation concentration

*24 experiments performed*
*after 2 hours of propagation*
*E = 0 V/MSE ; T = 20°*

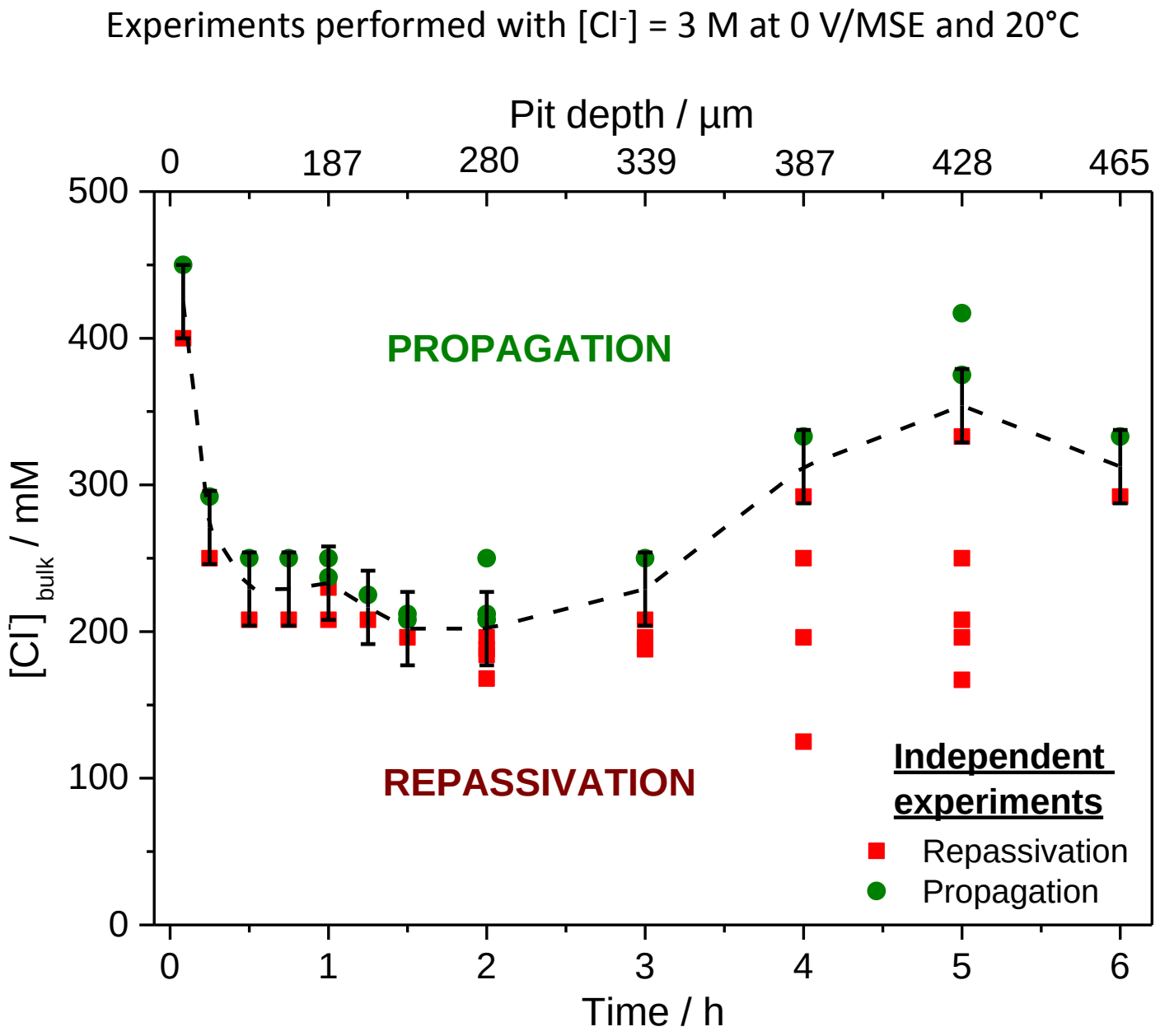
| [$Cl^-$] / mM | Propagation | Repassivation |
|---|---|---|
| 170 | | 1 exp |
| 180 | | 1 exp |
| 190 | | 4 exp |
| 200 | 2 exp → 40 % | 3 exp → 60 % |
| 210 | 7 exp → 78 % | 2 exp → 22 % |
| 250 | 4 exp | |

*18 experiments performed*
*after 5 hours of propagation*
*E = 0 V/MSE ; T = 20°*

| [$Cl^-$] / mM | Propagation | Repassivation |
|---|---|---|
| 170 | | 1 exp |
| 190 | | 1 exp |
| 210 | | 6 exp |
| 250 | | 2 exp |
| 333 | | 3 exp |
| 375 | 4 exp | |
| 420 | 1 exp | |

The repassivation concentration measurements are reproducible

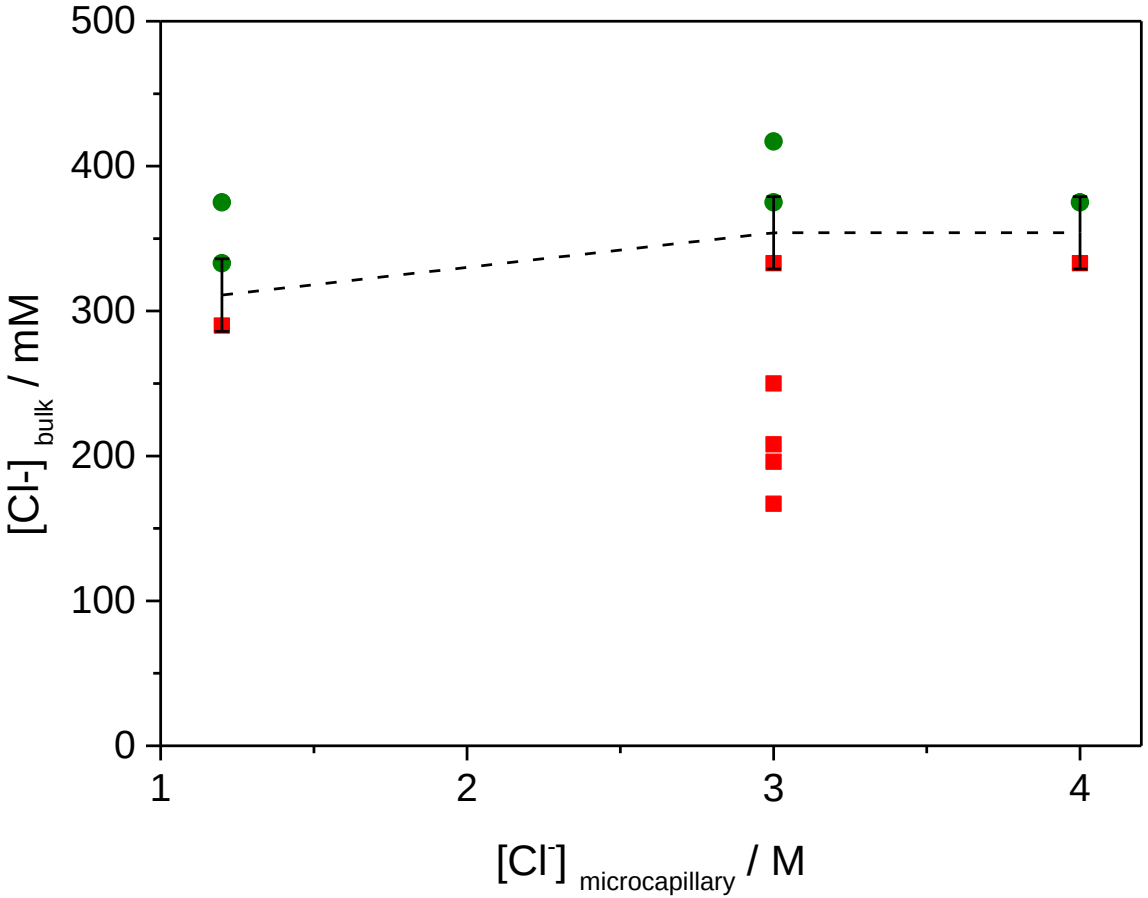
# Time evolution of the repassivation concentration



# Influence of $[Cl^-]_{microcapillary}$ on the repassivation concentration

Experiments performed at 0 V/MSE – 20° injecting different chloride concentrations with the microcapillary for 5 hours of propagation

Flow rate: 5.4 µL/h → 27 µL injected during 5 hours of propagation << 40 mL bulk

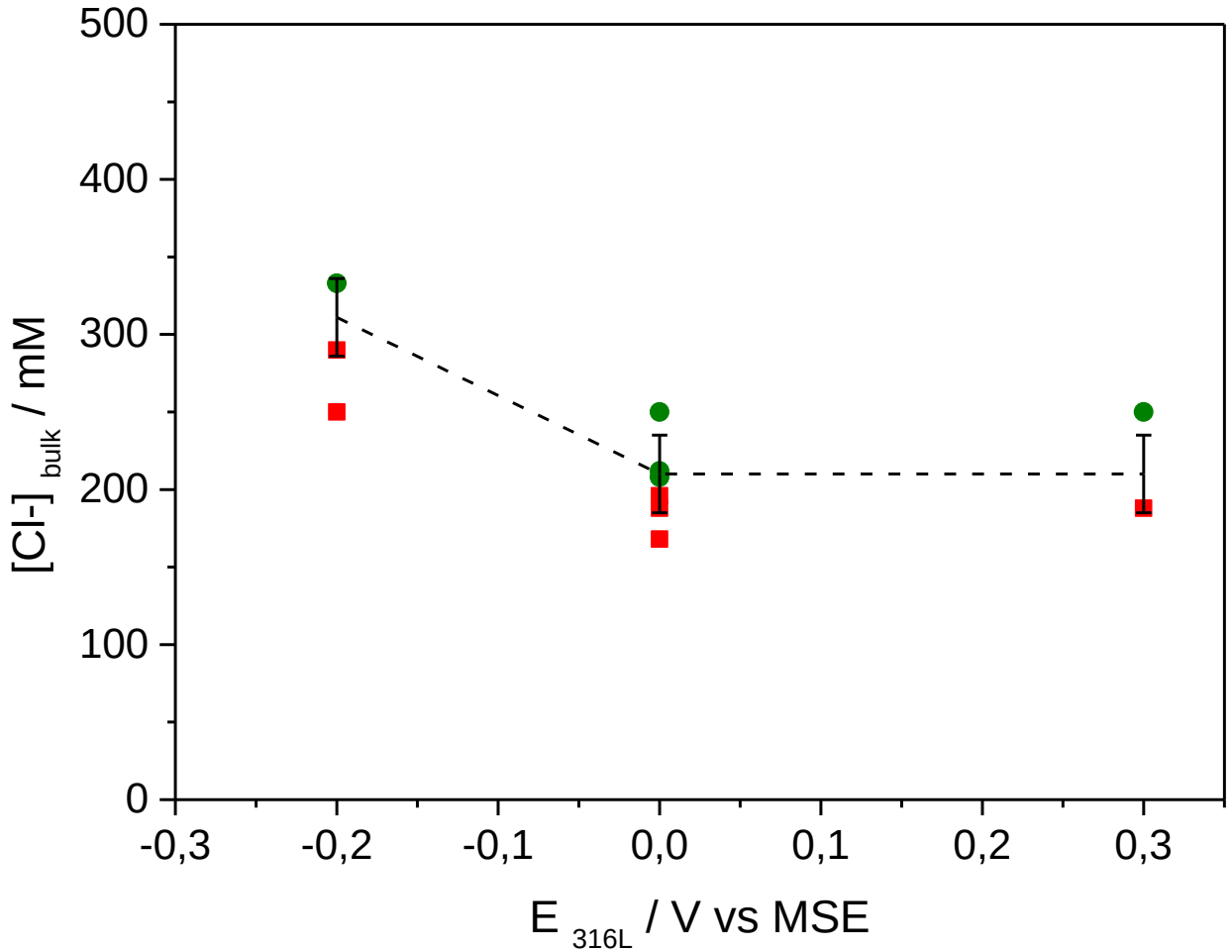



Negligible effect of $[Cl^-]$ injected by the microcapillary

# Influence of potential on the repassivation concentration

20° - 2 hours of propagation - $[Cl^-]_{microcapillary}$: 3 M - Flow rate: 5.4 µL/h

Experiments for different applied potentials in the passive domain




Higher repassivation concentration in the beginning of the passive domain

# Comparison with the existing work about repassivation potential

The repassivation potential is constant when a critical pit depth is reached

Literature: Determination of the dependence of $E_{rep}$ on $[Cl^-]_{bulk}$

- *S. Tsujikawa and al., 1987 :*
  304L in NaCl solution

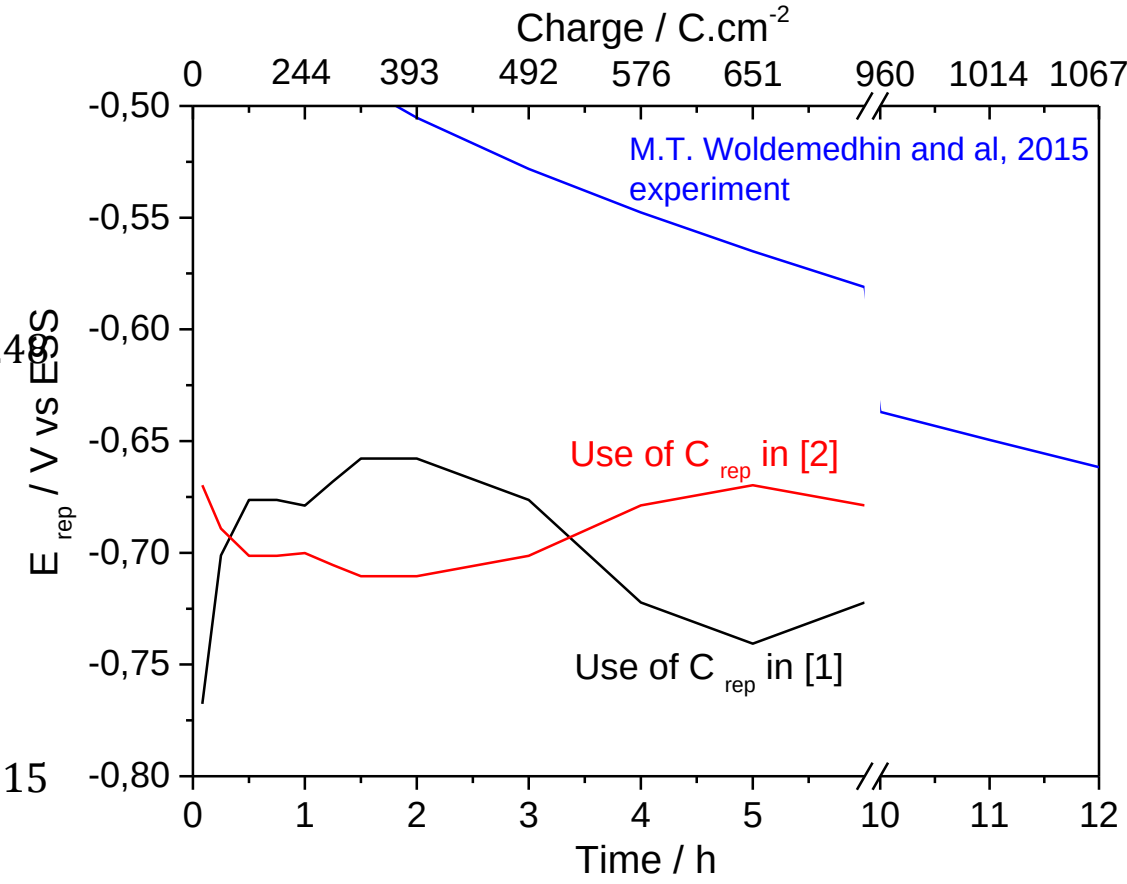
  Relation [1]

$$E_{rep}(V(SCE)) = -0.34 * log[Cl^-](mol.L^{-1}) - 0.48$$

- *M.T. Woldemedhin and al., 2015 :*
  316L in $FeCl_3$

  Relation [2]

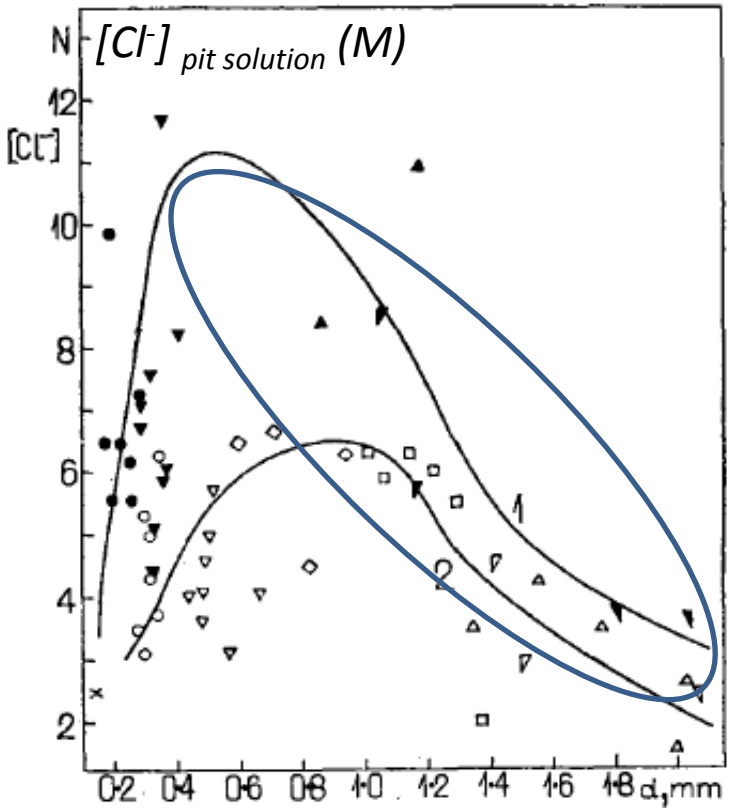
$$E_{rep}(mV(SCE)) = 55.8 * log[FeCl_3](mol.L^{-1}) - 215$$
$$\sim 55.8 * log[Fe^{3+}][Cl^-]^3(mol.L^{-1}) - 215$$



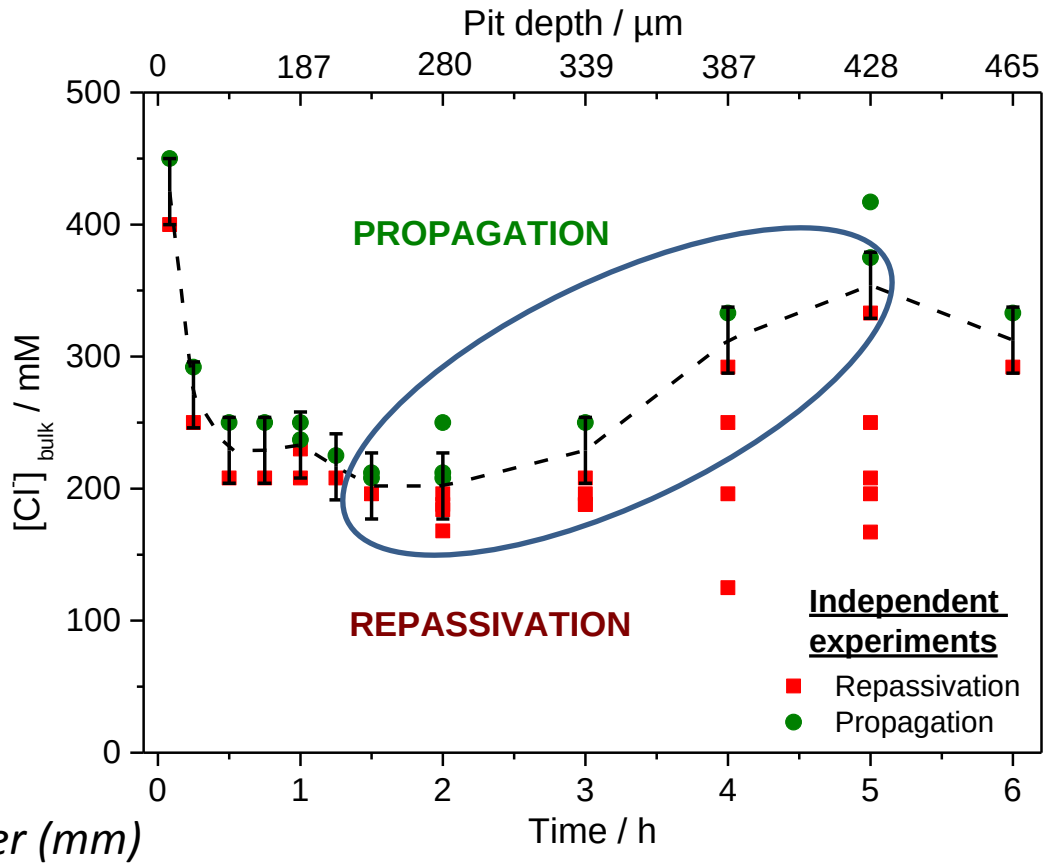

$C_{rep}$ measurements consistant with a constant $E_{rep}$

# Literature : evolution of [$Cl^-$] in the pit solution

*J. Mankowski and Z. Szklarska-Smialowska, 1975*: determination of $[Cl^-]_{pit\ solution}$ by freezing the pit solution with solid $CO_2$




*Pit diameter (mm)*




Decrease of [$Cl^-$] in the pit solution while the pit is propagating

→ Link with the increase of $C_{rep}$ above 350 µm ?

Research in progress: In-situ determination of $[Cl^-]_{pit\ solution}$ with microelectrodes

# Conclusions

- Initiation and propagation of a reproducible single pit on 316L stainless steel using a flow microcell setup

- Determination of single pit propagation mechanisms:
  - Pit bottom: diffusion
  - Pit mouth: potential control

- Important role of chloride ion in pitting corrosion processes

- Characterization of pit repassivation by bulk chloride concentration
  - Definition of a repassivation concentration $C_{rep}$
  - Reproducible measurement
  - Evolution of $C_{rep}$ with pit depth (for 20° - 0 V/MSE) :
    - Below 120 µm: decrease of $C_{rep}$
    - Between 120 µm and 350 µm: constant $C_{rep}$
    - Above 350 µm: increase of $C_{rep}$
  - No influence of $[Cl^-]_{microcapillary}$ on $C_{rep}$
  - Higher $C_{rep}$ at the beginning of the passive range


Thank you for your attention