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Evaluation of permanent embeddable reference electrodes in solution and concrete specimen

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Evaluation of Permanent Embeddable Reference Electrodes in Solution and Concrete Specimen

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INTRODUCTION

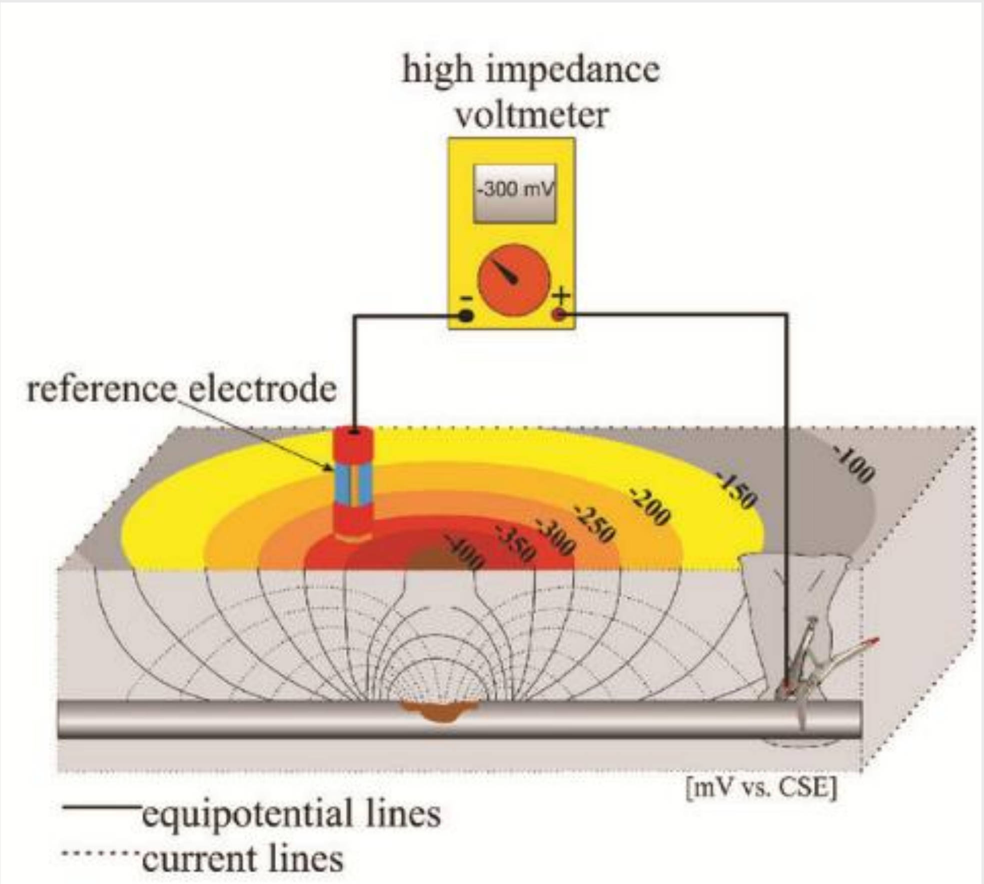
Monitoring atmospherically exposed reinforced concrete structures enables **corrosion risk assessment of steel reinforcement** (rebar) and supports optimized maintenance strategies.

Corrosion risk in concrete structures is typically assessed through inspections *focusing on key parameters such as the* ***open-circuit potential*** *(**OCP**) of rebar, electric resistivity, and the presence of aggressive agents such as chloride.*

Despite the widespread use of embedded electrodes for early corrosion detection in concrete, their application in Brazil remains limited due to high import costs and limited knowledge.

OCP: electrochemical measurement carried out with a **reference electrode (RE)** and a multimeter:

Typically performed on the concrete surface, following a predefined grid pattern, enabling the construction of potential maps that help identify areas of active corrosion. Widely used in the laboratory to evaluate the corrosion behavior of metals under controlled conditions.



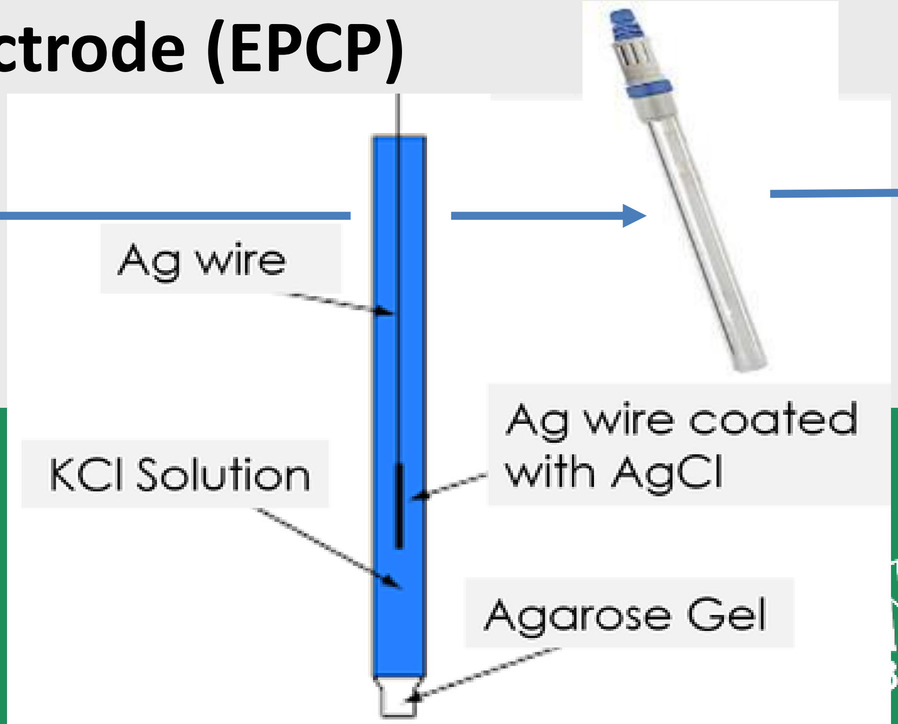
EBELL; BURKERT; MIETZ. (2018)

Reference Electrode - RE: stable and reproducible potential (true electrodes) for environmental metal behavior evaluation.

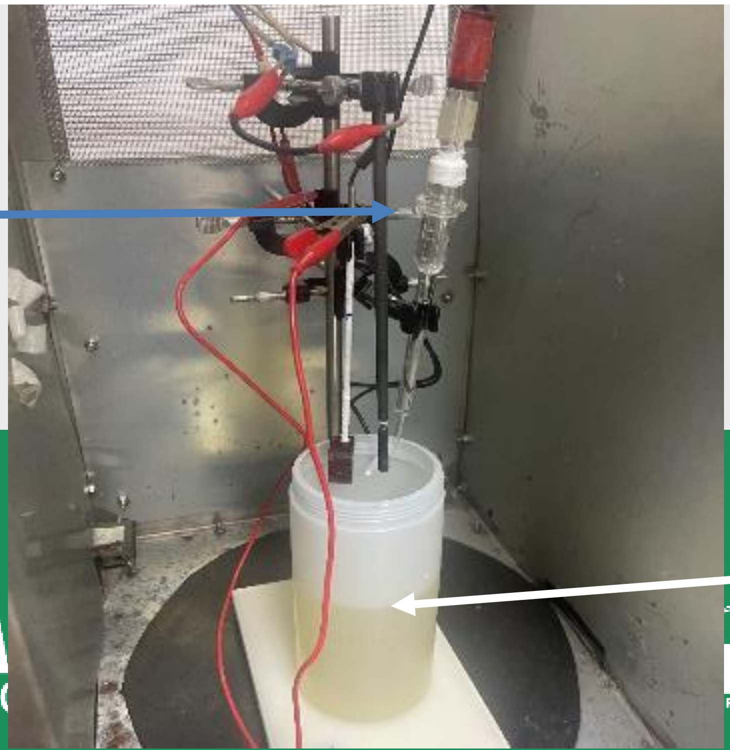
OCP MEASUREMENT ON THE CONCRETE SURFACE

Cu|$CuSO_4$ Electrode

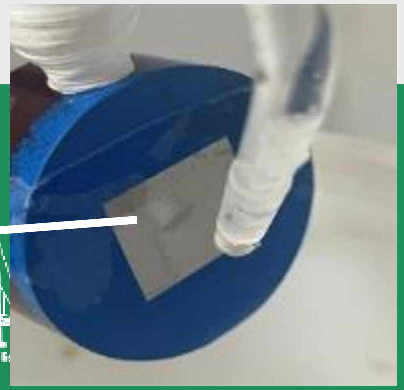
Ag/AgCl Electrode (EPCP)



OCP MEASUREMENT IN THE LABORATORY



Metal specimen in solution



Embedded Reference Electrode - ERE:

- ✓ **True electrode**, *despite presenting a low degree of variation;*
- ✓ **Pseudo-reference electrode**, *inherent precision limitations. Often used due to their durability and suitability for continuous rebar monitoring.*

ERE: 3 types evaluated in this study:

IMPORTED MODELS

EPCP (silver)

Ag|AgCl|KCl 0.5 mol/L

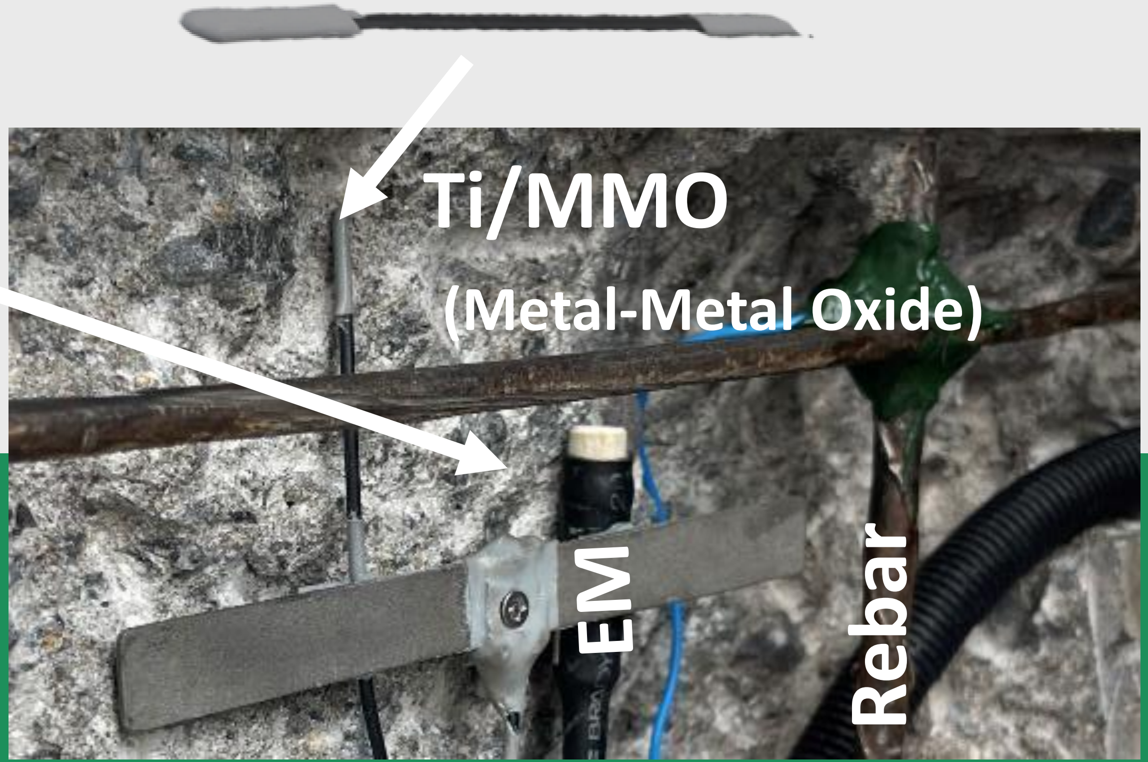
EM (manganese oxide)

MnO_2|NaOH 0.5 mol/L

LOCALLY PRODUCED SOLID MODEL

EMMO (titanium)

Ti/MMO wire from the inert anode mesh used in cathodic protection



OBJECTIVE

This study aims to evaluate the behavior of two imported embedded reference electrodes (**ERE**s) — **EPCP** (silver) and **EM** (manganese oxide) — and one locally produced electrode — **EMMO** (titanium), with a primary focus on their **established relative potentials in solution** and their **application in rebar monitoring** (ER), through **LABORATORY TESTING:**

- ✓ **ASSESSMENT TEST** BASED ON THE ABNT NBR 11105: **measure the ERE**s **relative potential** to the *Standard Hydrogen Electrode (SHE);*
- ✓ **CYCLIC POTENTIODYNAMIC CURVES**: analyze the behavior of **ERE**s to small amplitude currents;
- ✓ **IMMERSION TESTS***:* **long-term monitoring of ERE**s **relative potential** to an external silver reference electrode (*Ag|AgCl|KCl 3 mol/L, 210 mV vs SHE*) in solutions that **simulate changes in the concrete pore solution;**
- ✓ **CONCRETE SPECIMEN TEST (CS)***:* **long-term OCP monitoring** of **steel bars** to internal (embedded) and an external silver electrode *(Ag|AgCl|KCl 3 mol/L, 210 mV vs SHE).*

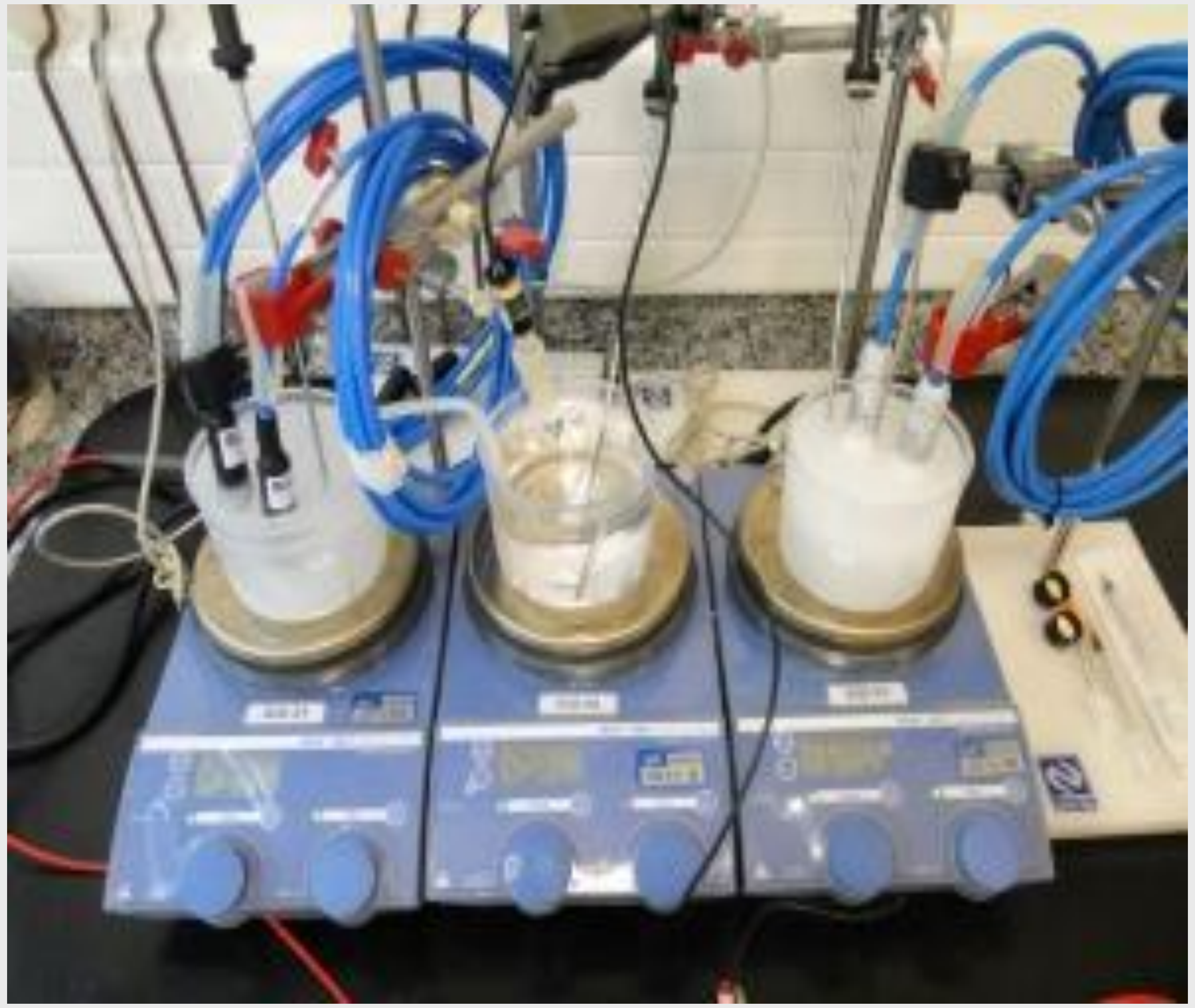
METHODS: ASSESSMENT TEST

***Conditions**:*

- **24 h of immersion** (23 °C ± 2 °C);
- **3 consecutive measurements at 5 min intervals** using a high impedance multimeter (>10 MΩ).

Immersion Solutions (manufacturers' technical specifications)*:*

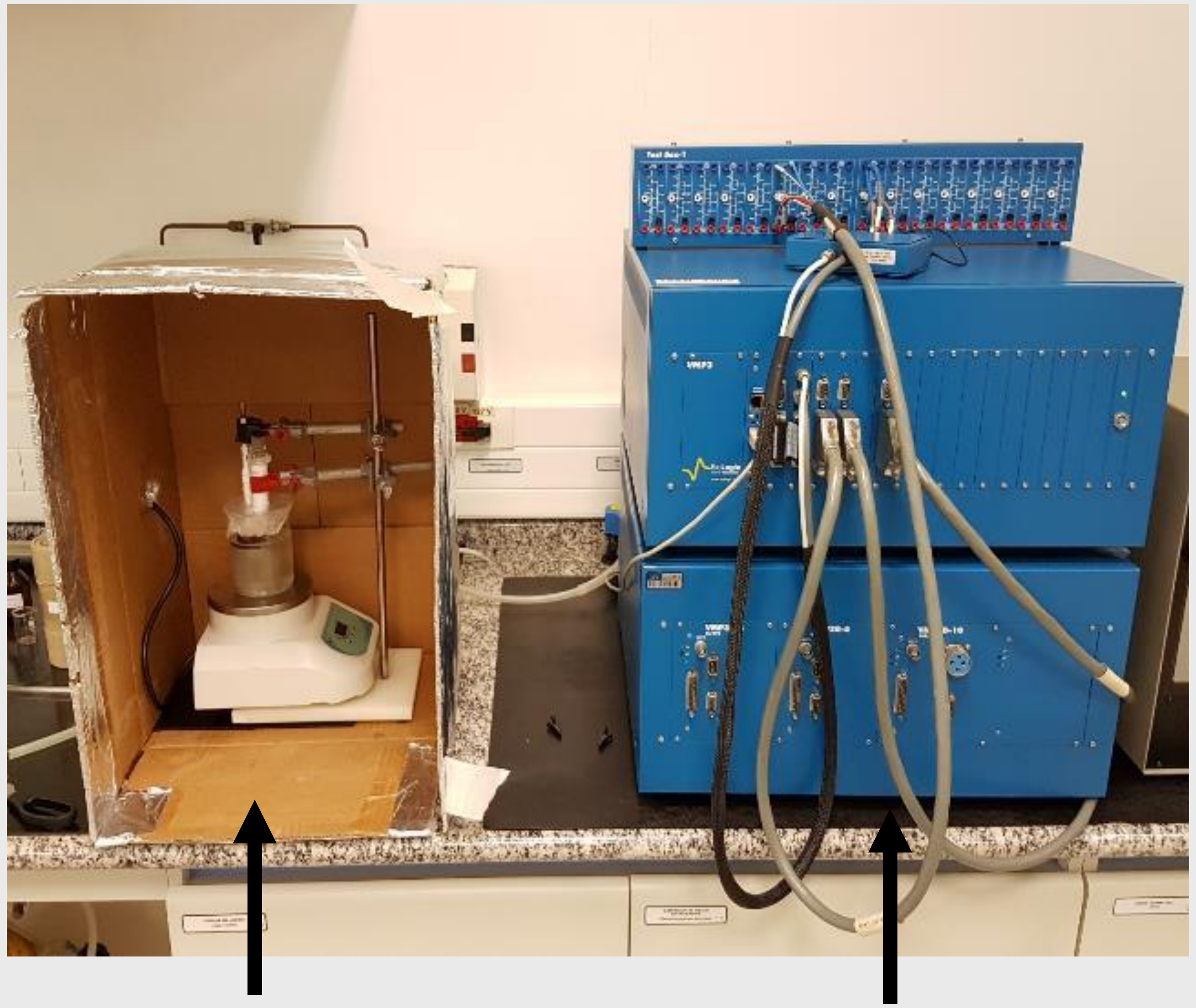
- **EM** and **EMMO**: **saturated calcium hydroxide solution** [$Ca(OH)_2$)];
- **EPCP**: sodium chloride solution (**NaCl** 0.5 mol/L).



METHODS: CYCLIC POTENTIODYNAMIC CURVES

Conditions:

- **24 h of immersion** in the exact solution of the assessment test (23 °C ± 2 °C) for **OCP stability**;
- Cyclic scans applied with **± 20 mV over voltage around the OCP**;
- Scans **started cathodically, followed by anodic** after 1 min



Corrosion cell - EREs in solution

Potentiostat equipment

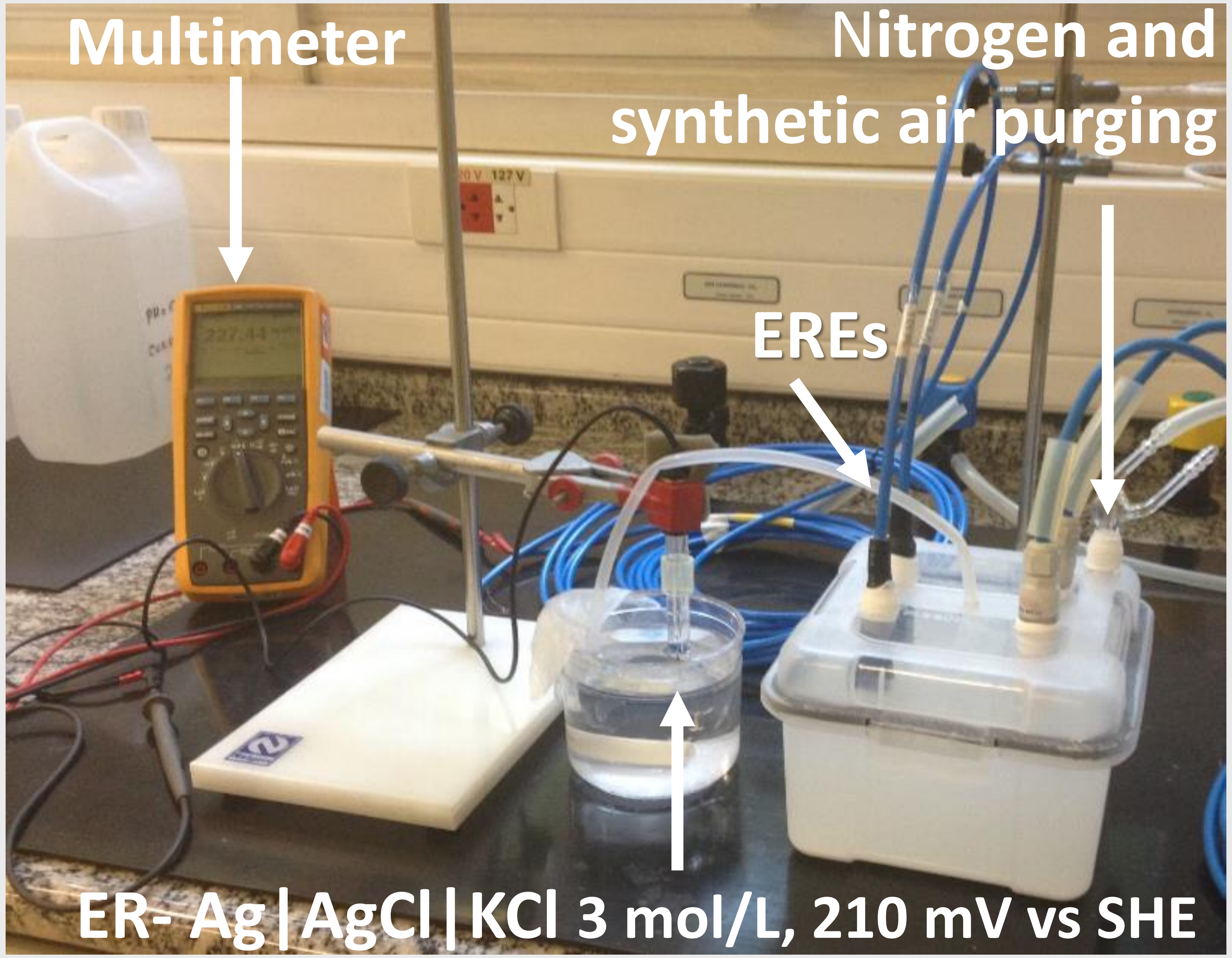
METHODS: IMMERSION TEST

Non-contaminated Concrete solution:

- High alkalinity: **$Ca(OH)_2$, pH 12.5** - 160 days;
- High alkalinity with oxygen variation: **24 h deaeration/aeration cycles, purging nitrogen and synthetic air** - 25 days.

Contaminated Concrete Solution:

- **Carbonated**: $Ca(OH)_2$, **pH adjusted to 9.5** (via Na_2CO_3) - 100 days;
- **Chloride-contaminated**: High alkalinity solution with **0.4 % sodium chloride** (NaCl) - 90 days.



METHODS: CONCRETE SPECIMEN TEST (OCP REBAR MONITORING)

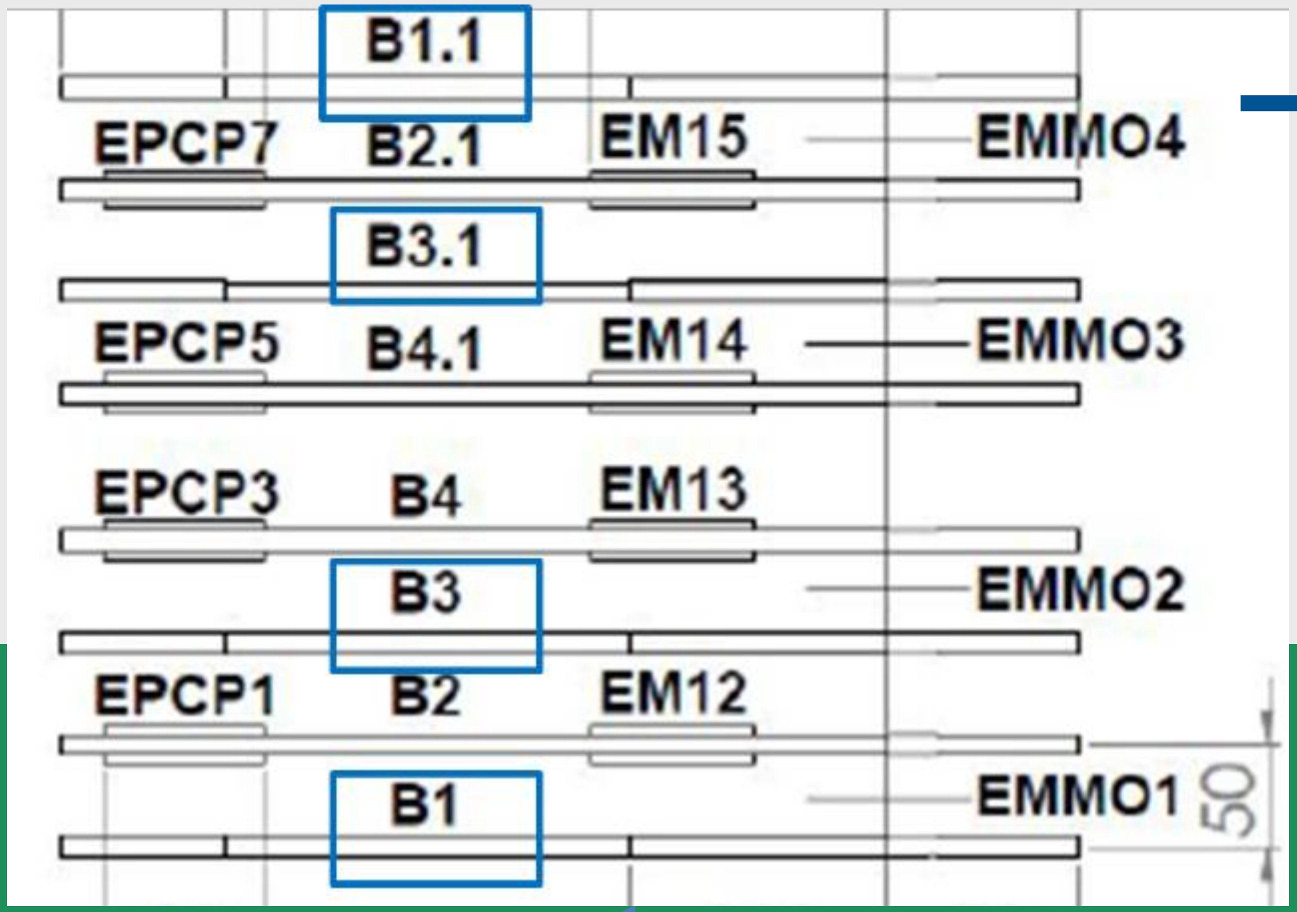
ERE configuration:

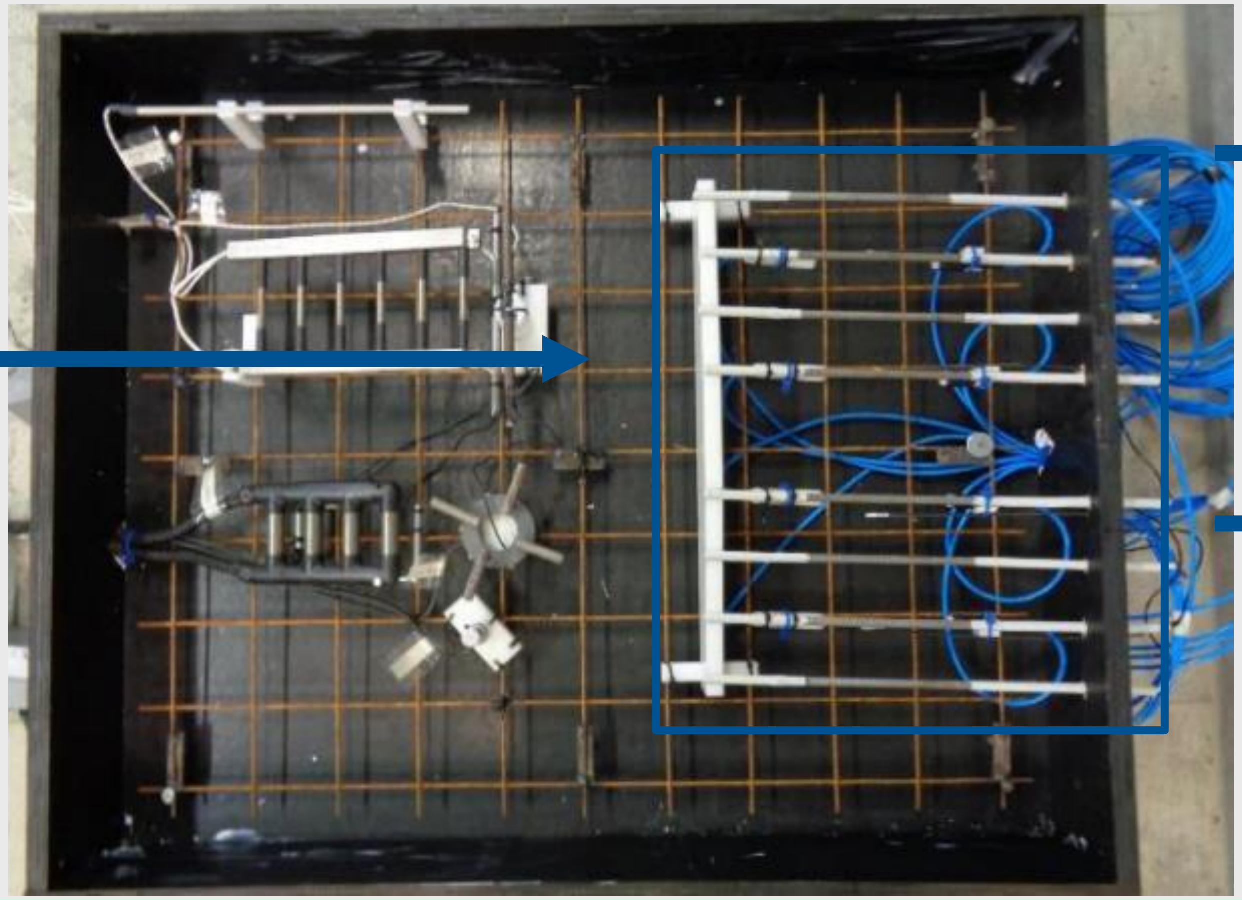
- **4 EM** and **4 EPCP** units fixed to two duplicate steel bars;
- **4 EMMO** units fixed to the formwork, near the bars.

Wetting and drying cycles (ASTM G109):

- **Cycles 1-3**: **$Ca(OH)_2$** solution *(non-contaminated condition);*
- **Cycle 4-13**: **3 % NaCl** solution *(chloride-contaminated condition).*

ERE TYPES AND IDENTIFICATION NUMBER





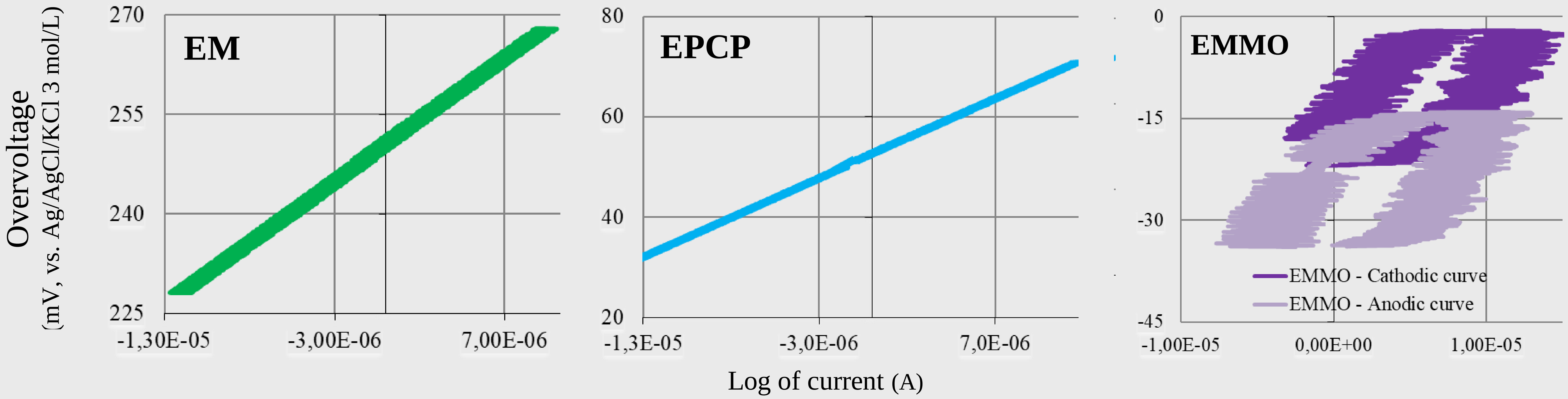
RESULTS - ASSESSMENT TEST

Electrode	EM ($Ca(OH)_2$ sat. solution)				EPCP (0.5 mol/L NaCl solution)				EMMO ($Ca(OH)_2$ sat. solution)				
Unit	**12**	**13**	**14**	**15**	**1**	**3**	**7**	**8**	**9**	**1**	**2**	**3**	**4**
Values (vs. SHE)	417	424	426	429	253	259	259	253	255	295	291	308	332
	418	428	427	431	254	260	260	255	258	296	291	310	333
	417	425	427	430	254	259	260	254	256	295	291	310	332
AV (vs. SHE)	**417**	**426**	**426**	**430**	**254**	**260**	**256**	**254**	**256**	**295**	**291**	**309**	**333**
OAV	**425 (SHE) 215 (Ag|AgCl|KCl 3 mol/L)**				**257 (SHE) 47 (Ag|AgCl|KCl 3 mol/L)**				**307 (SHE) 97 (Ag|AgCl|KCl 3 mol/L)**				
SD	5				2				17				

AV = Average Value; **OAV** = Overall Average value; **SD** = Standard Deviation

- ✓ **EM and EPCP electrodes** showed **low relative potential variation**, meeting the criteria (SD ≤ ±5 mV) for a **true reference electrode.** Behavior is **consistent with the manufacturer's specifications**.
- ✓ The **EMMO electrode** showed a **higher standard deviation** (SD = 17 mV), but still **acceptable** for a **pseudo-reference electrode.**

RESULTS - CYCLIC POTENTIODYNAMIC CURVES



EM and **EPCP** electrodes*:*

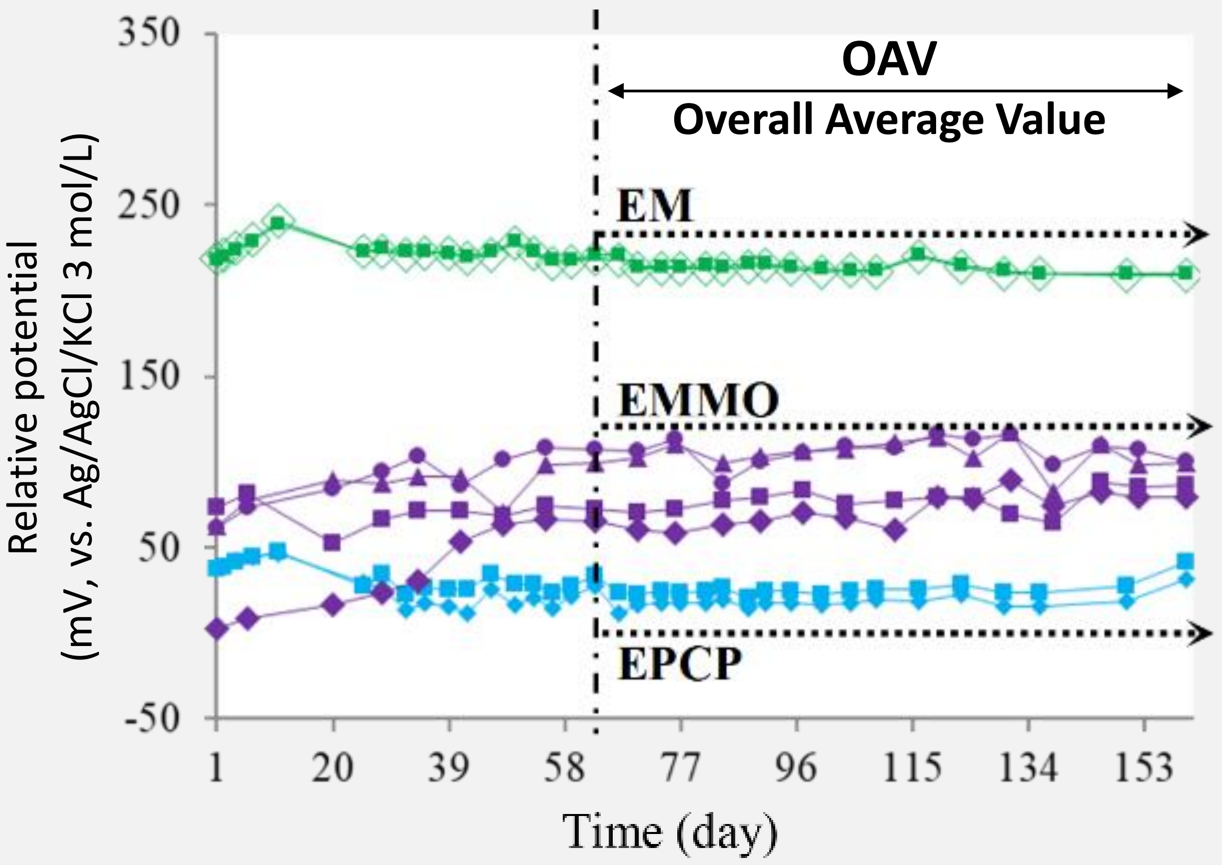
- Showed **linear, low-noise curves**;
- **Rapid potential shift and recovery**, confirming the **stability required of true electrodes.** Behavior is **consistent with the manufacturer's specifications**.

EMMO electrode*:*

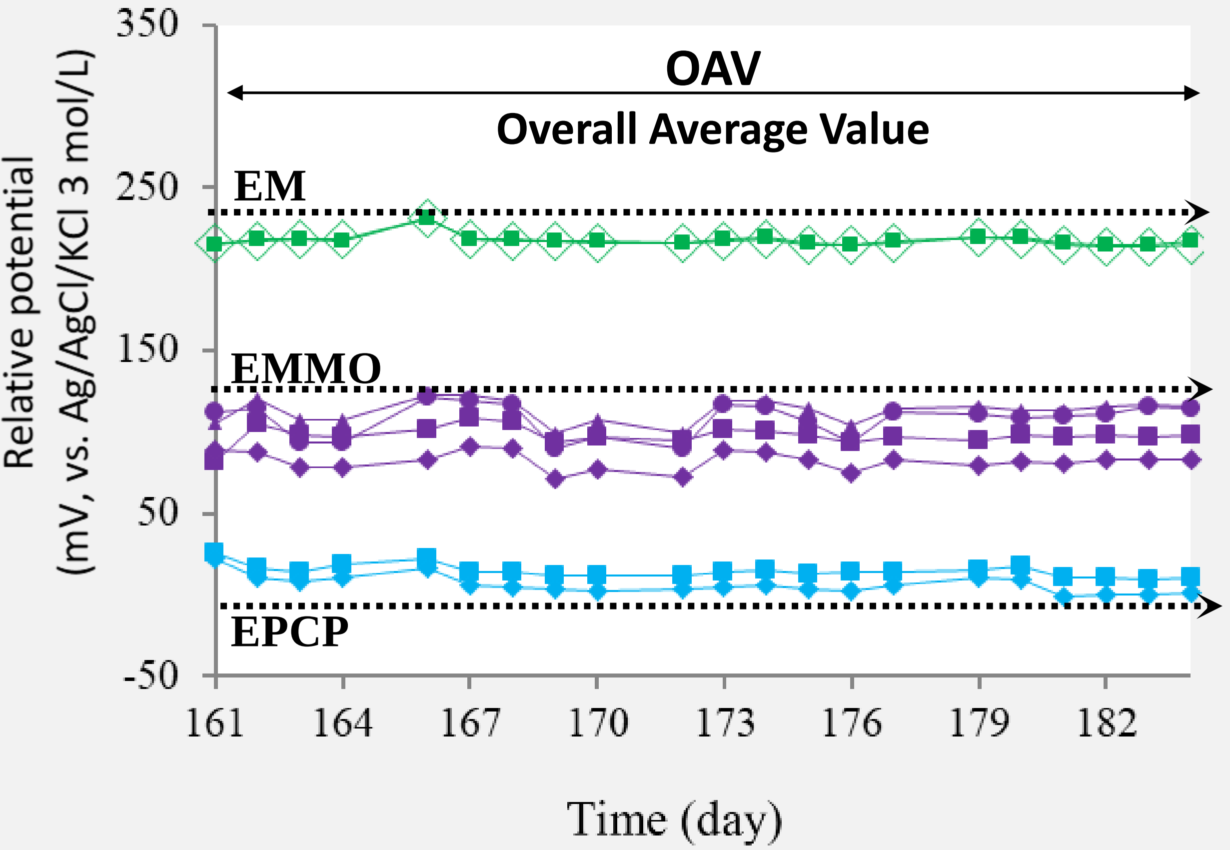
- Showed **hysteresis** and **noise, indicating instability** under small current perturbations;
- **Fails to meet** essential **criteria for true electrodes** (low polarization, fast recovery).

RESULTS - IMMERSION TEST

pH 12.5



pH 12.5 + O_2 variation



- ***pH 12.5***: EM and EPCP electrodes showed more **consistent behaviour. EMMO values between units have variation, considered stabilized after ~60 days** (time adopted for calculated OAV in immersion test)

EM: OAV assessment test 215 mV → 214 mV

EPCP: OAV assessment test (NaCl) 47 mV → 21 mV ***(decreased ~55 %)***

EMMO: OAV assessment test 97 mV → 90 mV

- ***pH 12.5 + O_2 variation*: all electrodes** showed **consistent behavior**

EM: OAV assessment test 215 mV → 217 mV

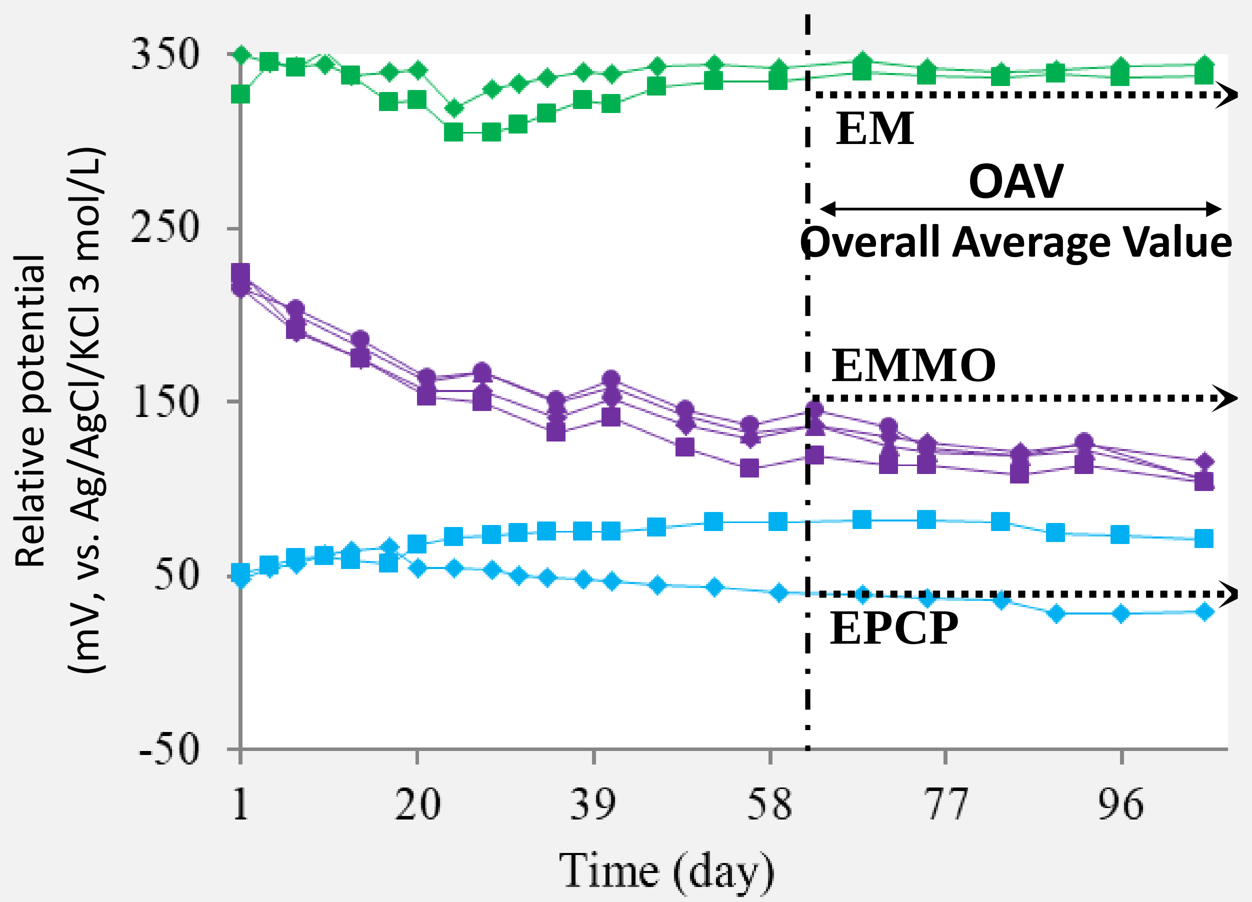
EPCP: OAV assessment test 47 mV (NaCl) → 10 mV ***(decreased ~78 %)***

EMMO: OAV assessment test 97 mV → 100 mV

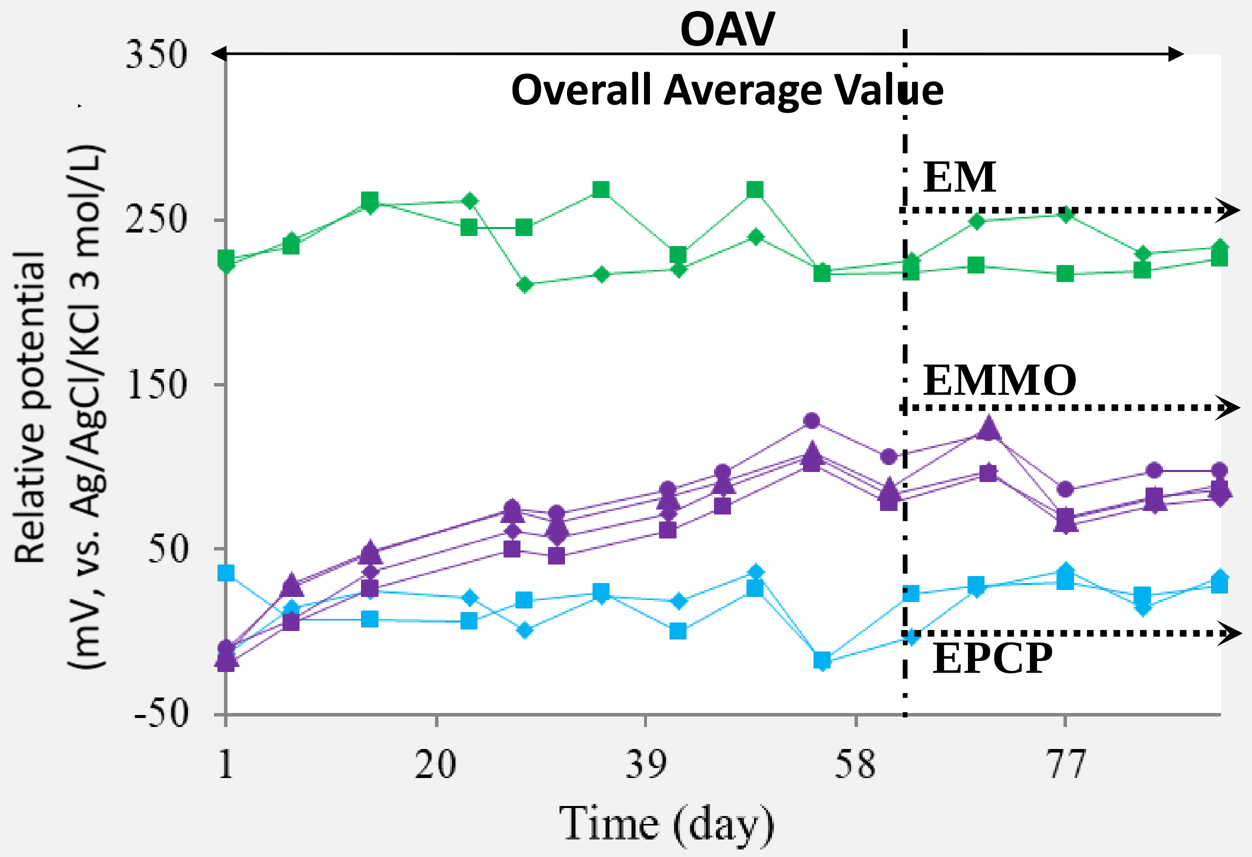
- In both solutions, the EM and EMMO showed good agreement between the results of the assessment and immersion tests. The EPCP presented a high percentage variation (≥ 55 %), but the value difference between tests was slight (< 37 mV).

EM and EMMO are more suitable for monitoring rebar in **non-contaminated** concrete, although EPCP can be used effectively.

pH 9.5



pH 12.5 + 0,4 % NaCl



- ***pH 9.5*: all electrodes** showed **increased potential** values **compared to all solutions**. EM exhibited the highest increase

  EM: OAV assessment test 215 mV → 340 mV ***(increased ~ 58 %)***

  EPCP: OAV assessment test (NaCl) 47 mV → 56 mV

  EMMO: OAV assessment test 97 mV → 118 mV

- ***pH 12.5 + NaCl*: EM and EPCP electrodes** showed an increase in potential values, and EMMO a slight reduction

  EM: OAV assessment test 215 mV → 229 mV

  EPCP: OAV assessment test 47 mV (NaCl) → 26 mV ***(decreased ~45 %)***

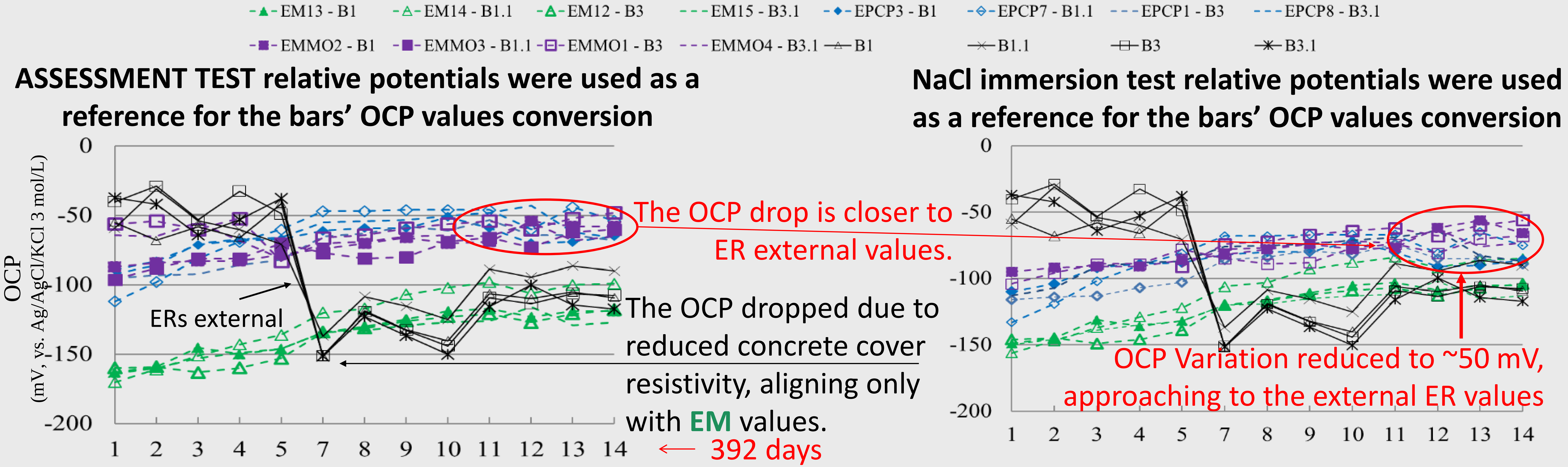
  EMMO: OAV assessment test 97 mV → 84 mV

- EMMO showed good agreement between the results of the assessment and immersion tests. For the EM, this correlation was observed only in the chloride-containing solution. EPCP exhibited a high percentage variation (45%) in chloride solution; however, the absolute difference was small (< 20 mV).

EMMO and EPCP are more suitable for monitoring rebar in **contaminated** concrete. EM can significantly shift the relative potential of carbonated concrete

RESULTS - CONCRETE SPECIMEN TEST

OCP monitoring bars (B1/B1.1 and B3/B3.1) with EM, EPCP, EMMO, and an external electrode



The EREs showed consistent behavior. Maximum unit variations were 21 mV (**EM**), 40 mV (**EPCP**), and 17 mV (**EMMO**). Using the relative potential obtained in the immersion test for OCP conversion provides a more accurate interpretation than relying only on assessment test values.

PRINCIPAL CONCLUSIONS

ASSESSMENT TEST x IMMERSION TEST:

- ✓ The locally produced **EMMO** electrode demonstrated stable and consistent potential values across all test conditions. Both **EMMO** and **EPCP** proved suitable for monitoring rebar in contaminated concrete. The **EM** electrode showed significant potential shifts in carbonated concrete, which may affect its reliability in corrosion risk assessment.

CONCRETE SPECIMEN TEST:

- ✓ The test demonstrated the stability and reproducibility of **EREs**, aligning with immersion test trends. The relative potential obtained in the immersion test in chloride solution provides a more accurate interpretation of rebar **OCP** values.

In practice, corrosion risk monitoring using **EREs** focuses on tracking potential trends, especially identifying significant drops in rebar **OCP** values. Nevertheless, it is recommended to periodically verify the relative potential of **EREs** against a conventional true reference electrode placed on the concrete surface, both to check their long-term stability and particularly as chloride or carbonation fronts significantly advance in the concrete cover.

CONSIDERATIONS: CONCEPTUAL DESIGN PHASE

- ✓ Plan **electrode networks** during the conceptual design phase, based on **structural layout and anticipated corrosion risks**
- ✓ **Cables** should be **embedded in the concrete**, with **terminals routed to monitoring panels**
- ✓ **Panel** allows **manual OCP** readings or **automatic data collection and transmission**, enabling real-time analysis and data storage
- ✓ **Panel** placement must consider **accessibility** and **monitoring coverage**
- ✓ **No standards** define **minimum quantity, spacing, or layout** – consult a corrosion specialist
- ✓ For **existing structures**, field interventions are required. These **involve drilling through the concrete cover** to insert the reference electrode, **routing surface-mounted cables** to the monitoring panel, and sealing the opening with a cementitious material

Thank You

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