Assessing the susceptibility of a substrate to filiform corrosion without applying a paint layer

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Assessing the susceptibility of a substrate to filiform corrosion without applying a paint layer

European Aluminium Congress 2017

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National Research Council Canada

About NRC

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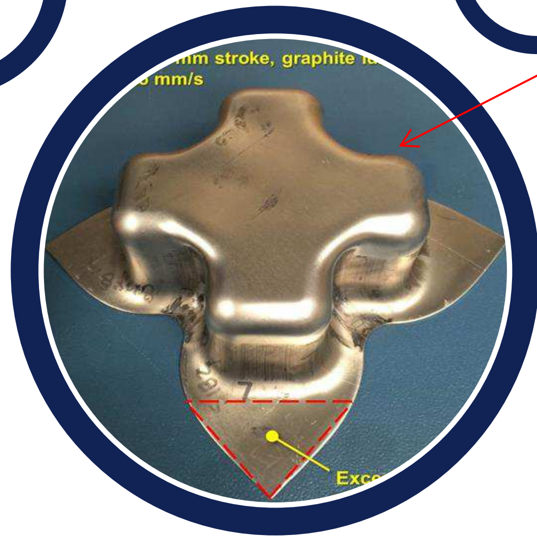
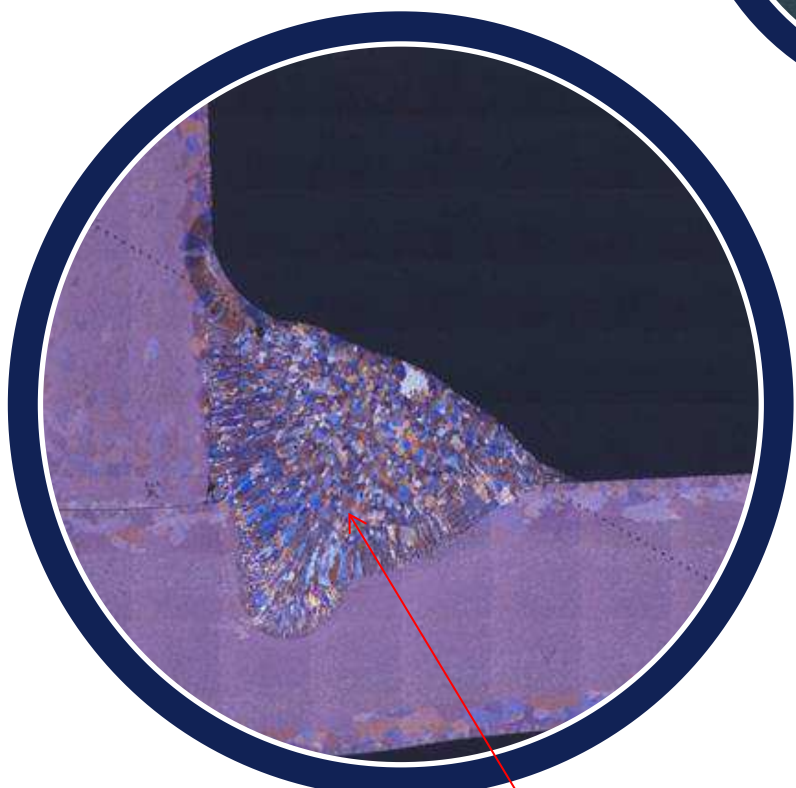
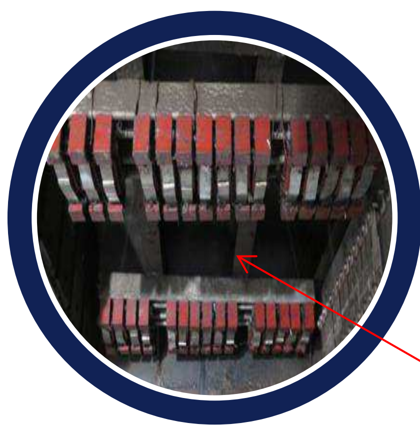
ALTec industrial R&D group – From 2015 to now



Forming:
Hot stamping, Casting, Extruding…





20 PROJECTS

6M$ +

INVESTED TO THE BENEFIT OF THE MEMBERS

Corrosion and durability:
SCC, galvanic corrosion, filiform corrosion, in-service exposure condition monitoring…

Assembling:
Welding (GMAW, laser, FSW…), Adhesives…

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ALTec partners

Rio Tinto

PRIMA

Économie, Science et Innovation Québec

alu Québec
Aluminium Cluster

Aluminium Association of Canada

Aluminium Valley Society

Réseau TRANS-Al Network

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ALTec Members (20 industrial members as of August 2017)

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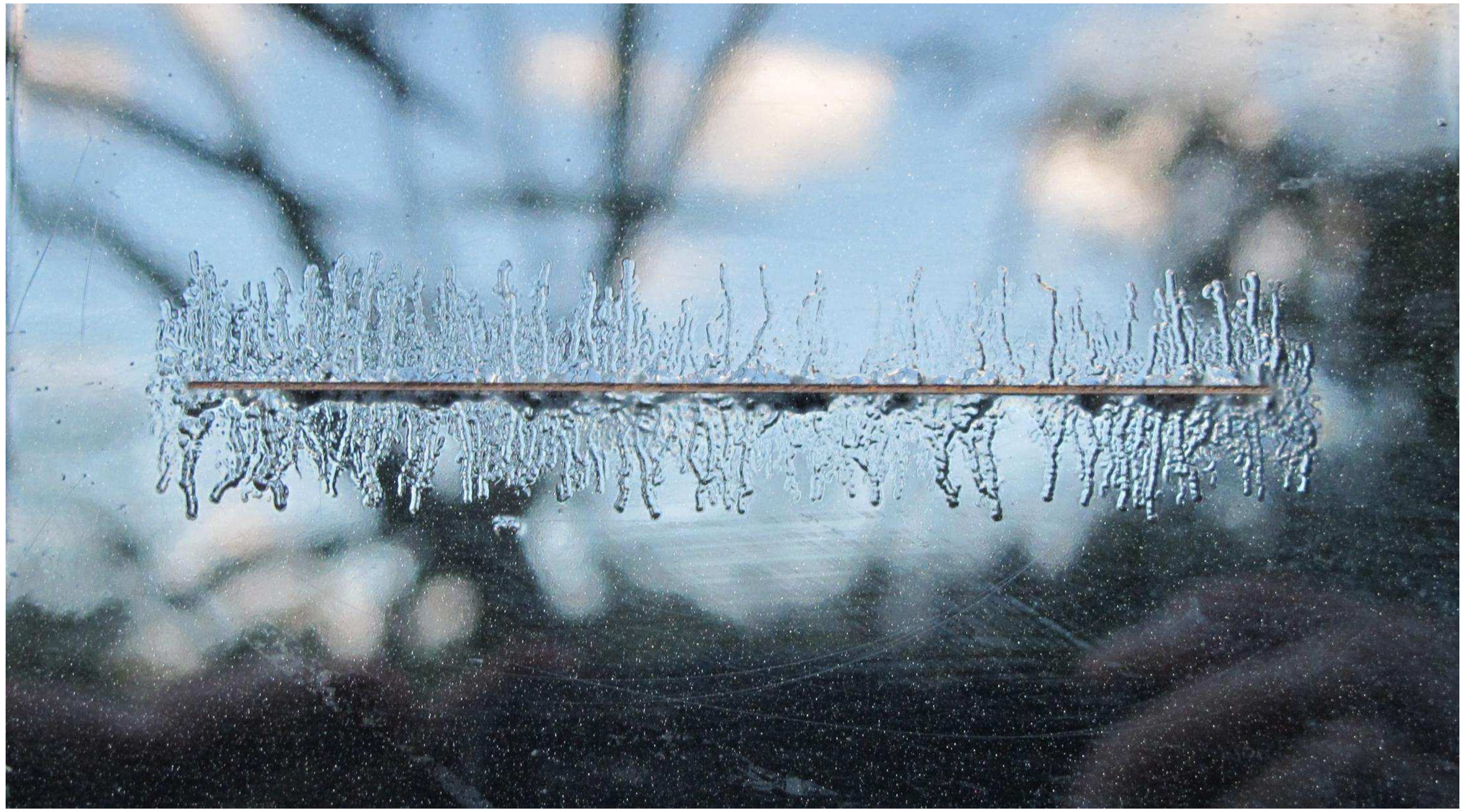
What is filiform corrosion?

- "Filiform corrosion is a type of localized corrosion which affects painted metals" that "gives rise to corrosion products of a filamentous appearance under coating."

A. Bautista / Progress in Organic Coatings 28 (1996) 49-58

- Occurs in humid but not saturated atmospheres, with relative humidity (RH) between 70 and 95%

J.L. Delplancke / Progress in Organic Coatings 43 (2001) 64-74



Why this project?

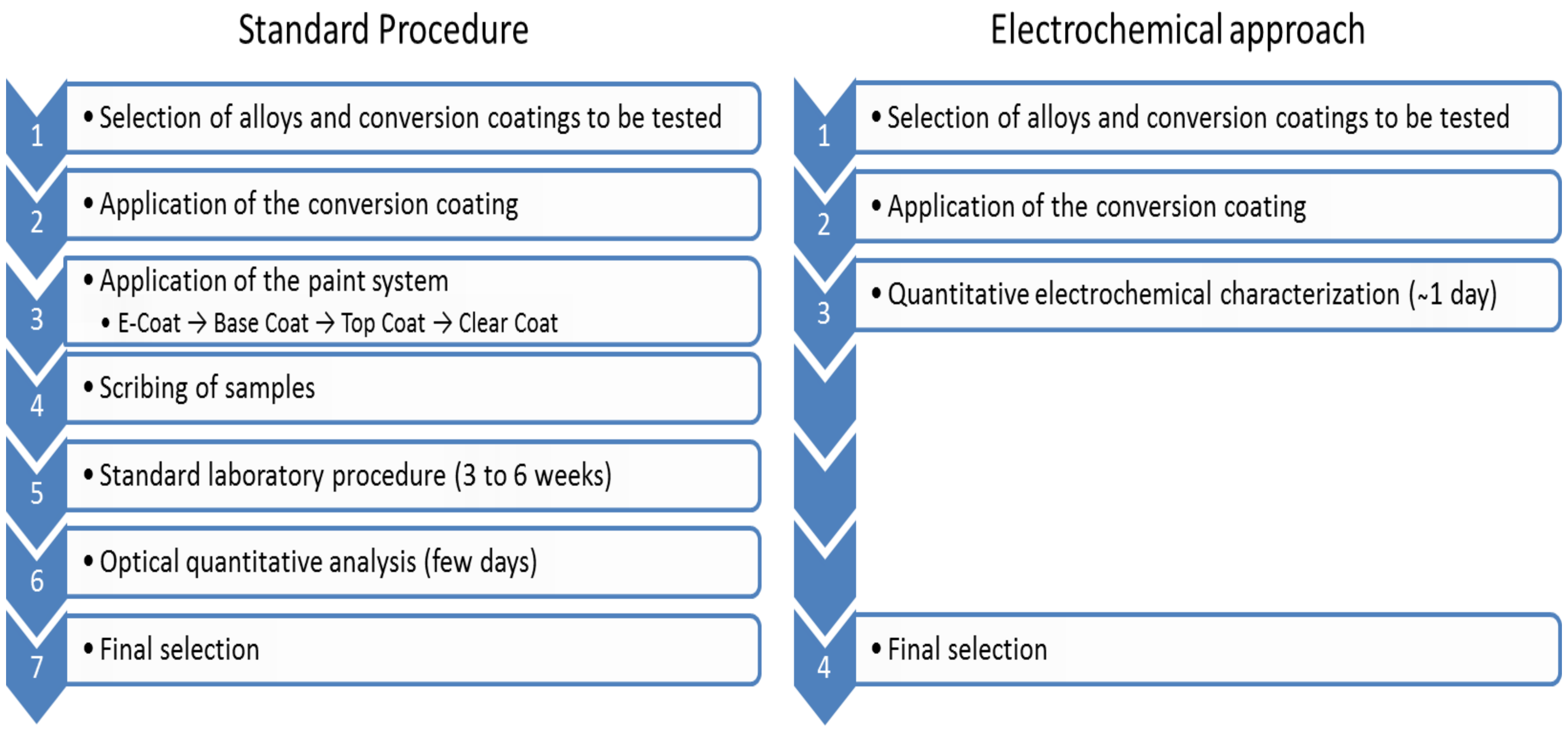
- Due to lightweighting efforts, there is a growing use of high yield strength alloys with noble elements
  $\Rightarrow$ Noble intermetallic: active for oxygen reduction reaction causing local galvanic coupling

- It is possible to develop alloys that are less sensitive to filiform corrosion by closely controlling there composition. However, the worldwide supply in raw materials (bauxite) and recycling can make it difficult and extremely expensive to control impurities that may cause filiform corrosion.

- In order to mitigate corrosion, one will use conversion coatings which are expensive:
  $\Rightarrow$ Following the Cr(VI) ban, which new product is suitable for your alloy?
  $\Rightarrow$ To which extent can we minimized this step?
  $\Rightarrow$ Can a fast test be used in production for quality control?

Objectives

Can we, with a fast electrochemical approach, predict the susceptibility of an alloy and/or an alloy/conversion coating couple to filiform conversion coating without the need for paint application?



TARGETED BENEFITS FOR ALTec MEMBERS

Reduction of direct and indirect costs related to filiform corrosion problems by:

- diminishing prototyping cost
- reducing time to market
- supplying a complementary tool for quality control
- decreasing risks associated with high production volume.

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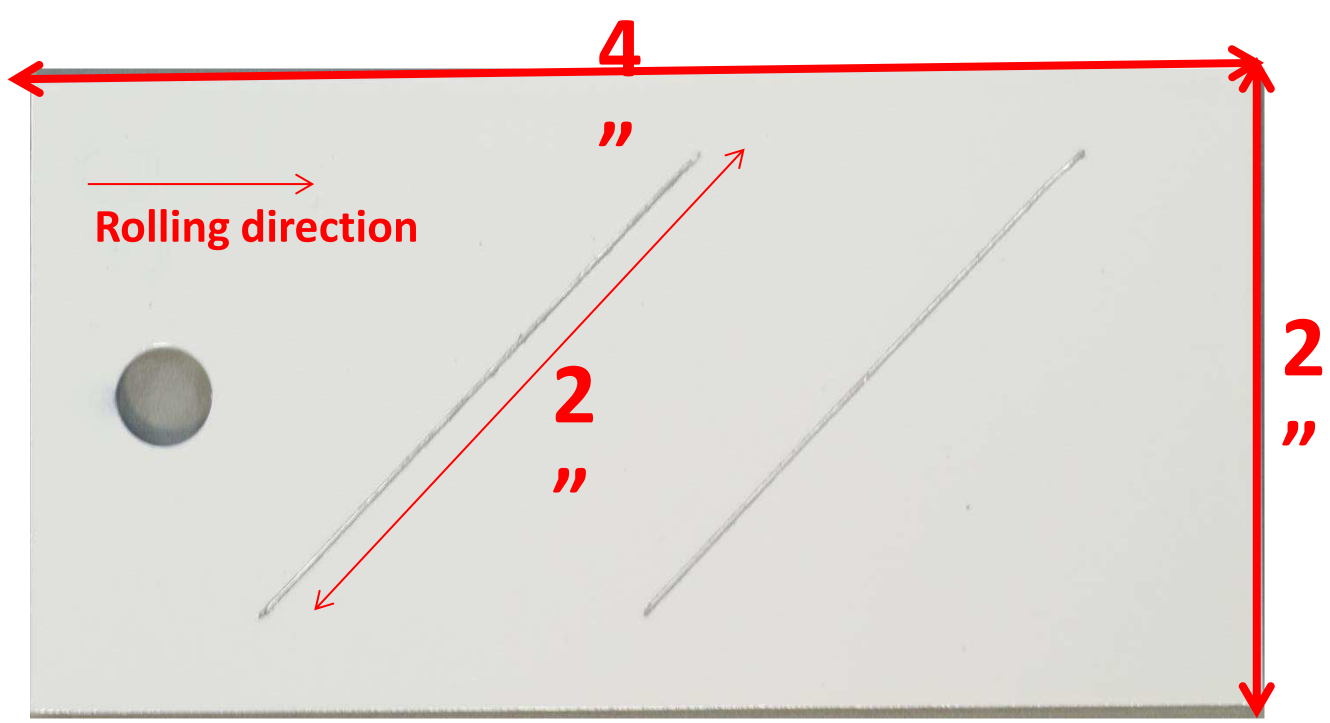
Phase 1: Sample preparation and establishment of a baseline

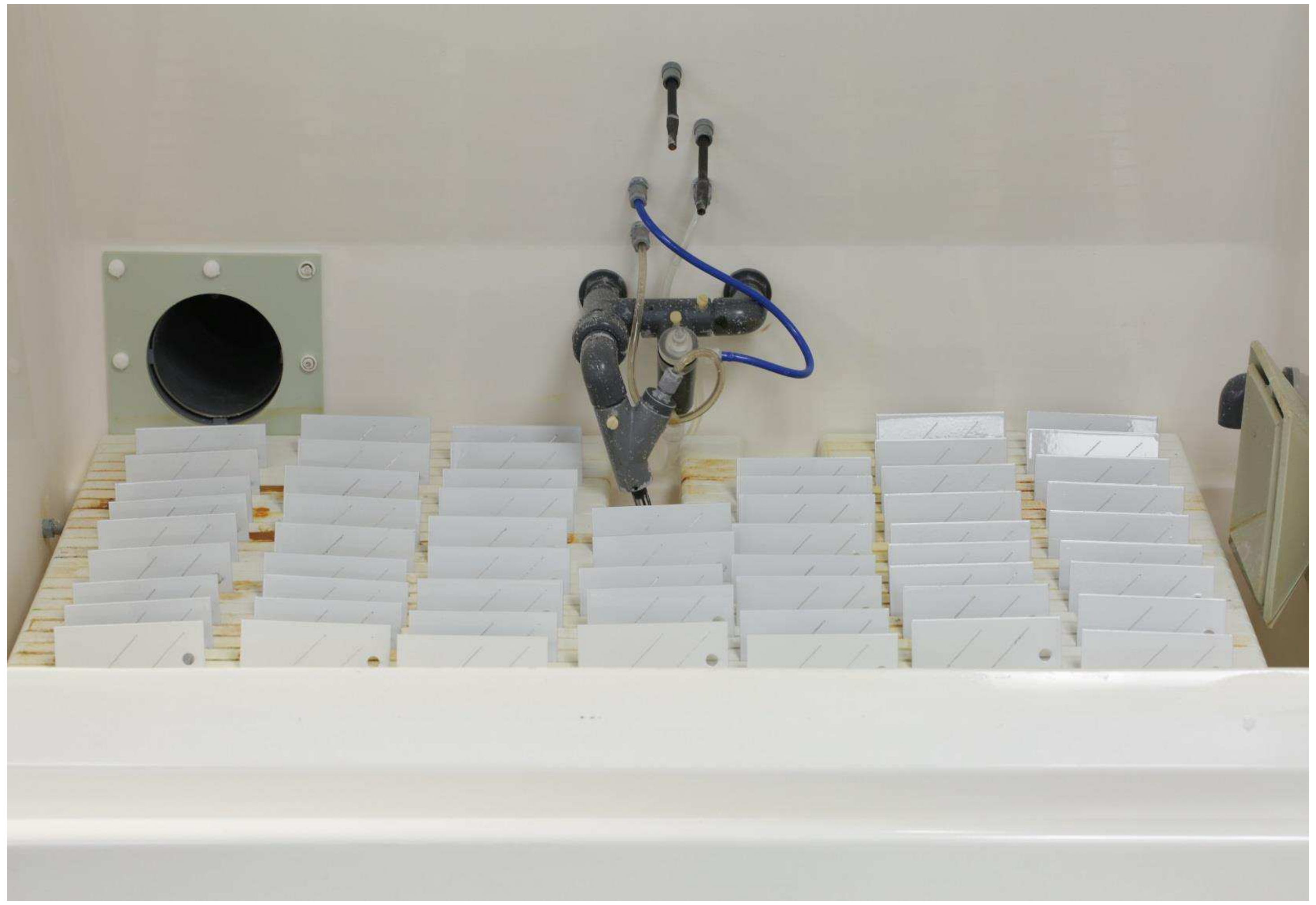
› A wide span test matrix:
  - 4 different substrates expected to corrode at different rates:
  - 5 different surface chemical preparation (conversion coatings (CC))
  - Full automotive paint system applied by ACT test panel

	AAn°1 grinded	AAn°1 as laminated	AAn°2 as laminated	AAn°3 as laminated
no-conversion coating - (alkaline clean, ecoat, prime, base, clear)	x	x	x	x
Zinc Phosphate with sealer plus ecoat, prime, base, clear	x	x	x	x
Zinc Phosphae without sealer plus ecoat, prime, base, clear	x	x	x	x
Zirconium based plus ecoat, prime, base, clear	x	x	x	x
Chromate plus ecoat, prime, base, clear	x	x	x	x

Phase 1: Sample preparation and establishment of a baseline

- Standard laboratory test that is known to correlate road exposure results
  - 60 samples tested : 3 samples x 20 AA/Conversion Coating combinations





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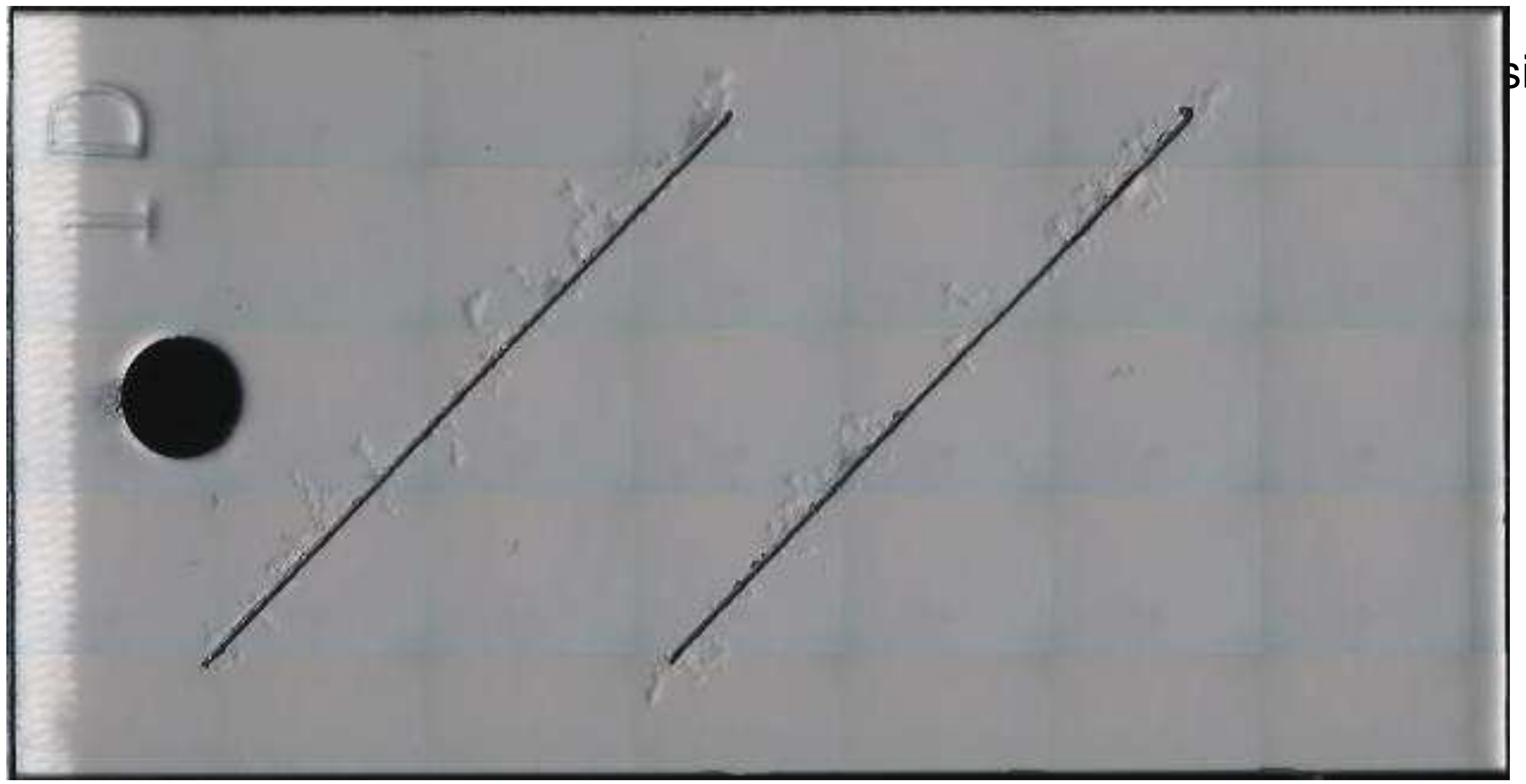
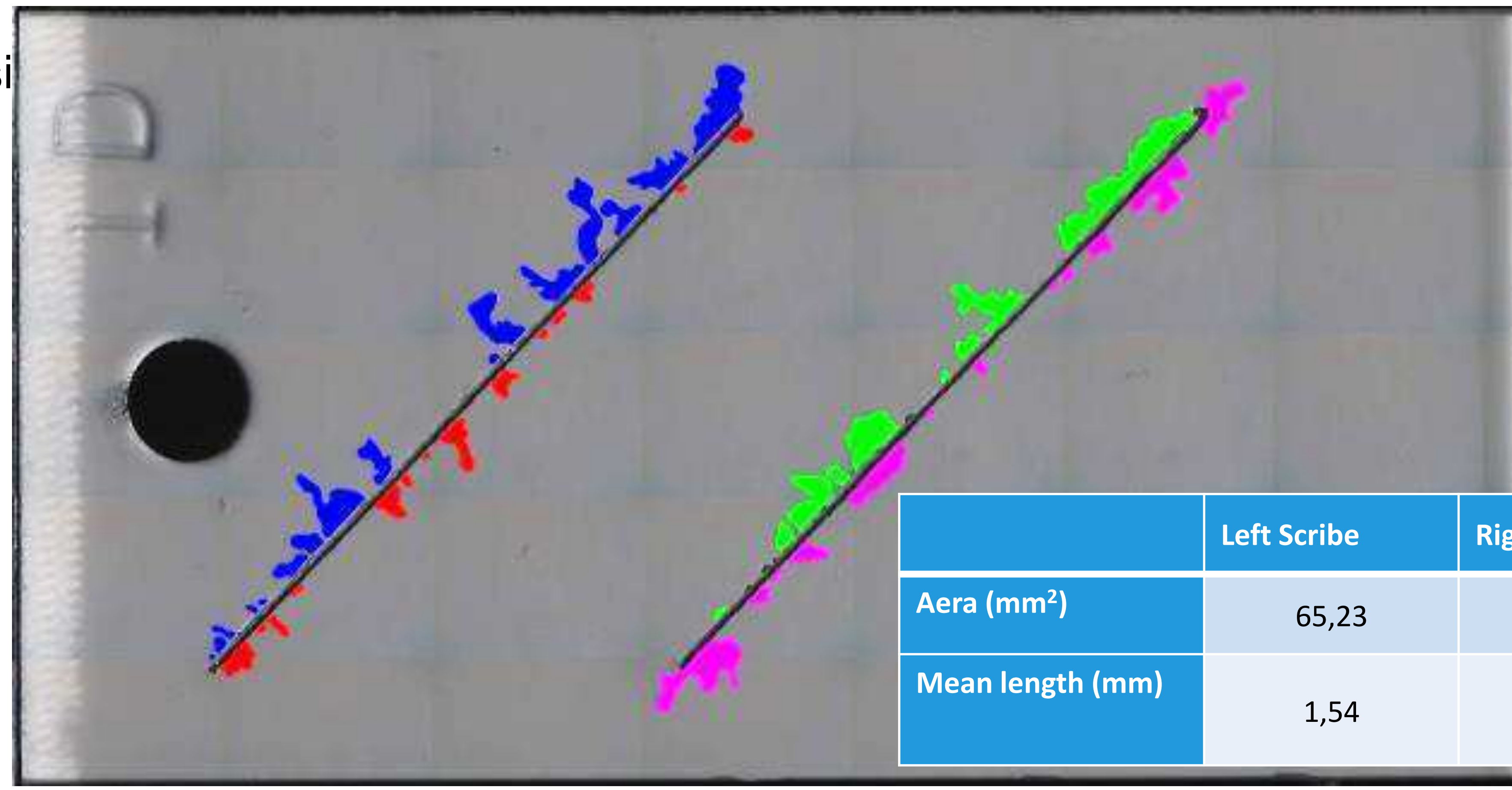
Phase 1: Sample preparation and establishment of a baseline

› Optical characterization of the corrosion extent:
  - Two parameters were extracted:
    - The corroded area
    - The length of the filiform

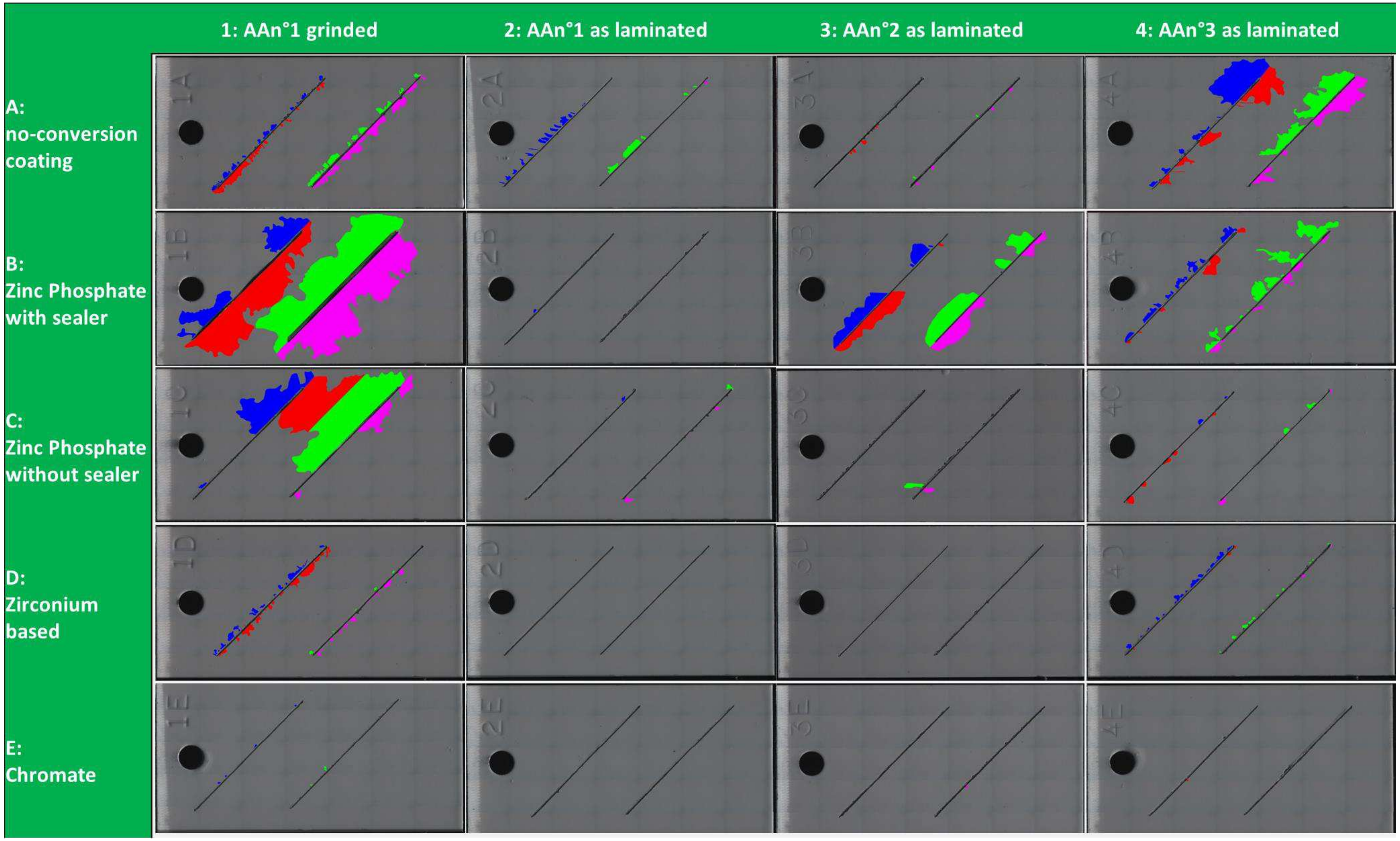




	Left Scribe	Right Scribe
Aera (mm²)	65,23	73,40
Mean length (mm)	1,54	1,29

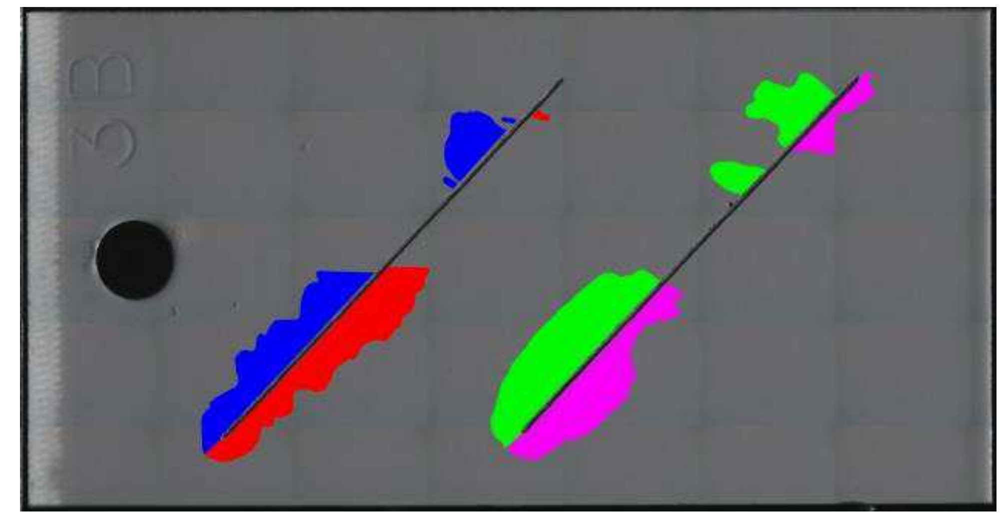
Phase 1: Sample preparation and establishment of a baseline

› Optical characterization of the corrosion extent:

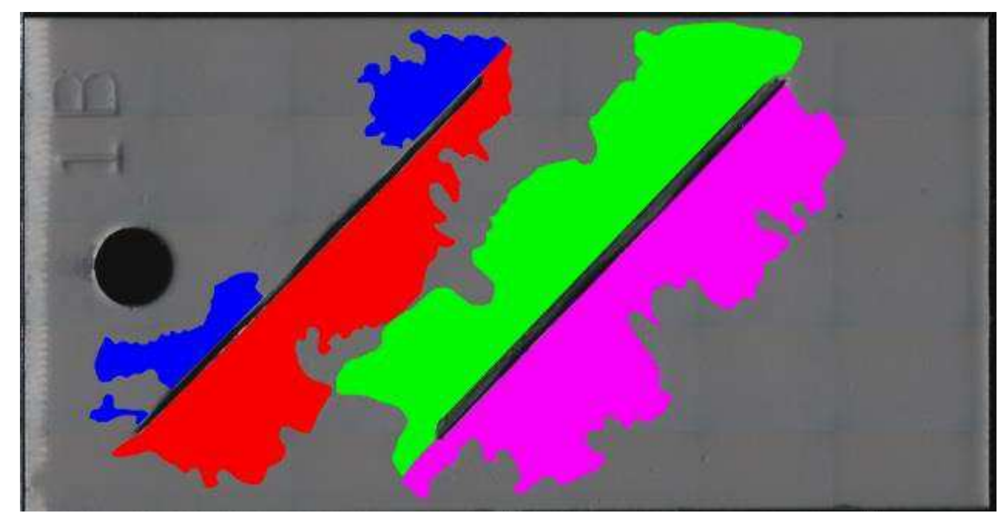


Various corrosion morphologies were observed

Large corroded area with extremely fine filaments parallel to the rolling direction.



Very large area of paint lifting: looks more like blisters or large interconnected filaments.



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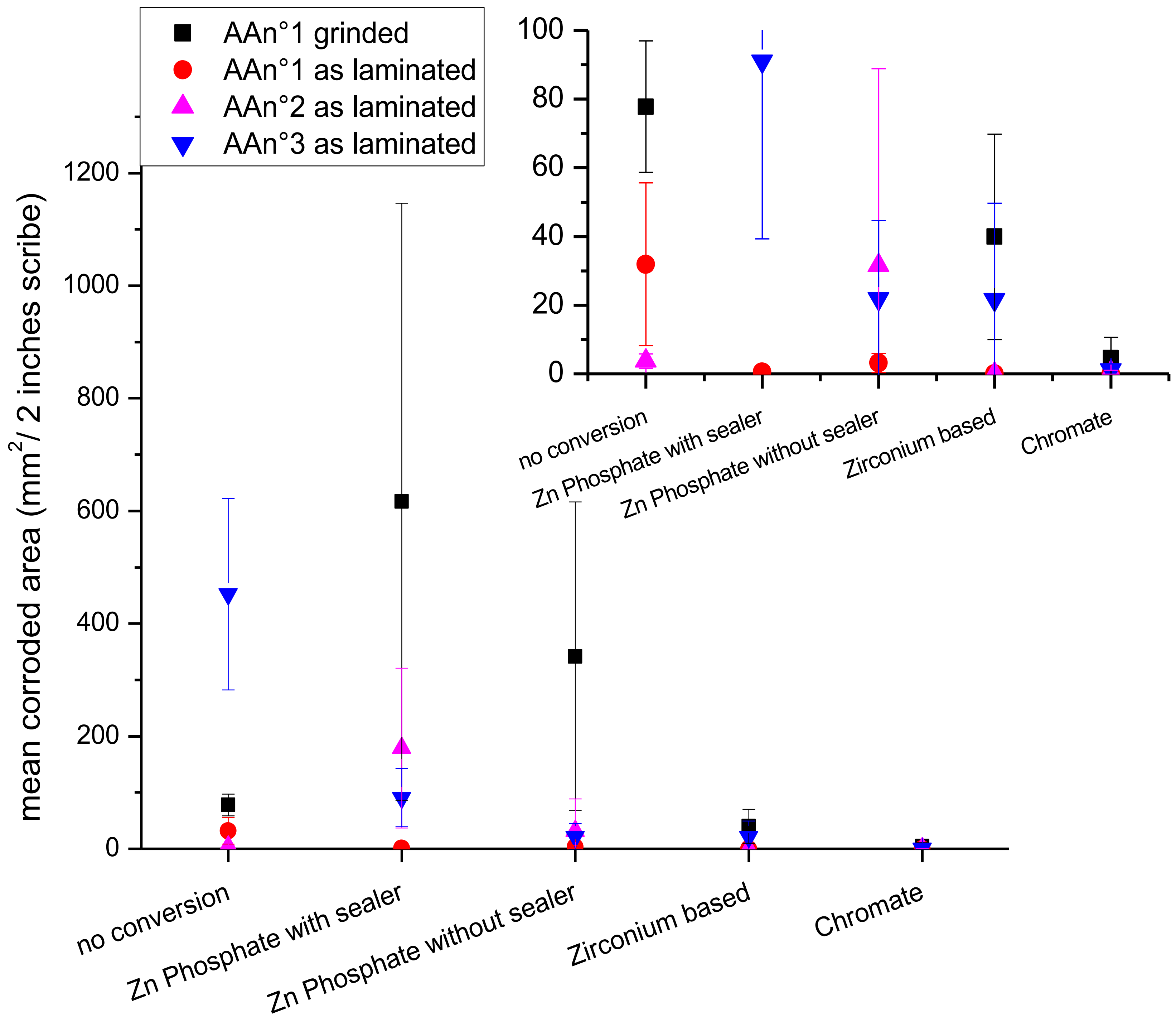
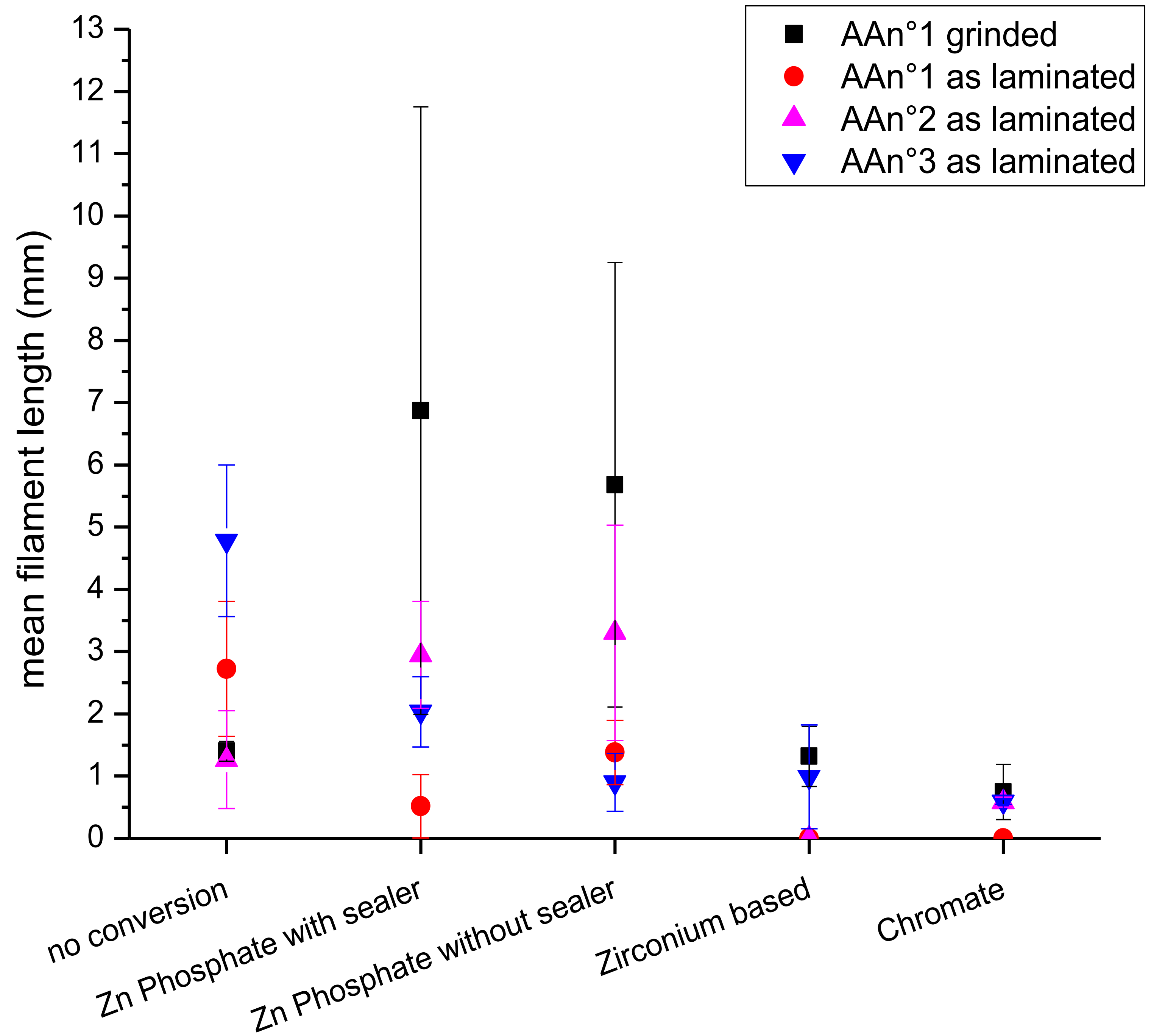
Phase 1: Sample preparation and establishment of a baseline

› Optical characterization of the corrosion extent:





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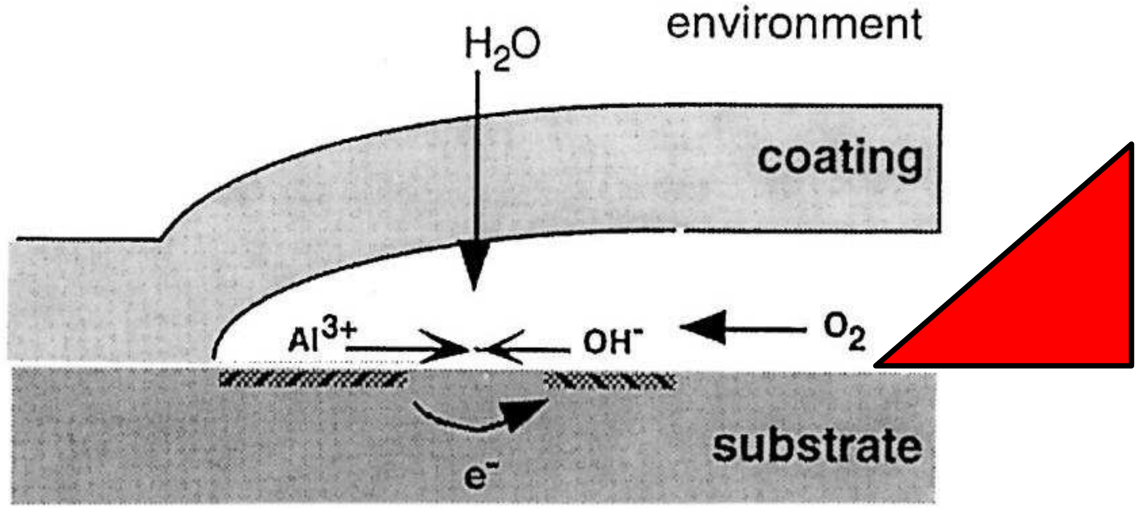
Phase 2: Electrochemical testing approach

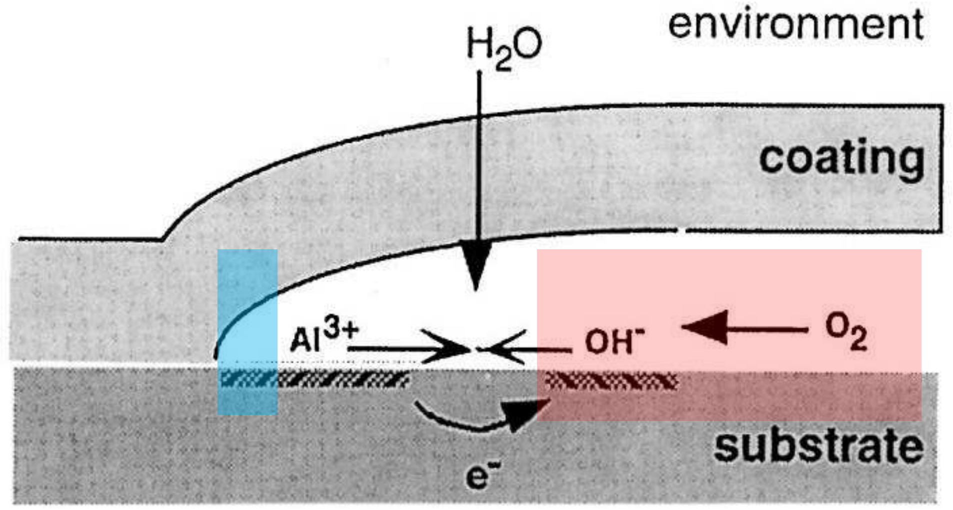
- Filiform corrosion is a process in two steps:
  - First step is the corrosion of the substrate at a defect of the paint which causes the paint to lift in the near by regions.



Initiation through a slight corrosion of the aluminum substrate through the penetration of a small amount of water and salt at a defect of the organic coating.

H. LEIDHEISER Jr., Corrosion, 38 (1982) 374.

  - Once the paint is lifted, this gives rise to conditions for a differential aeration corrosion (same as crevice corrosion, pitting corrosion…) that will cause the filiform to grow.



H. J . W. LENDERINK, PhD thesis, Delft University of Technology, The Netherlands, 1995.

Phase 2: Electrochemical testing approach

› Defining electrochemical parameters that are susceptible to correlate the corrosion observed on the painted samples:

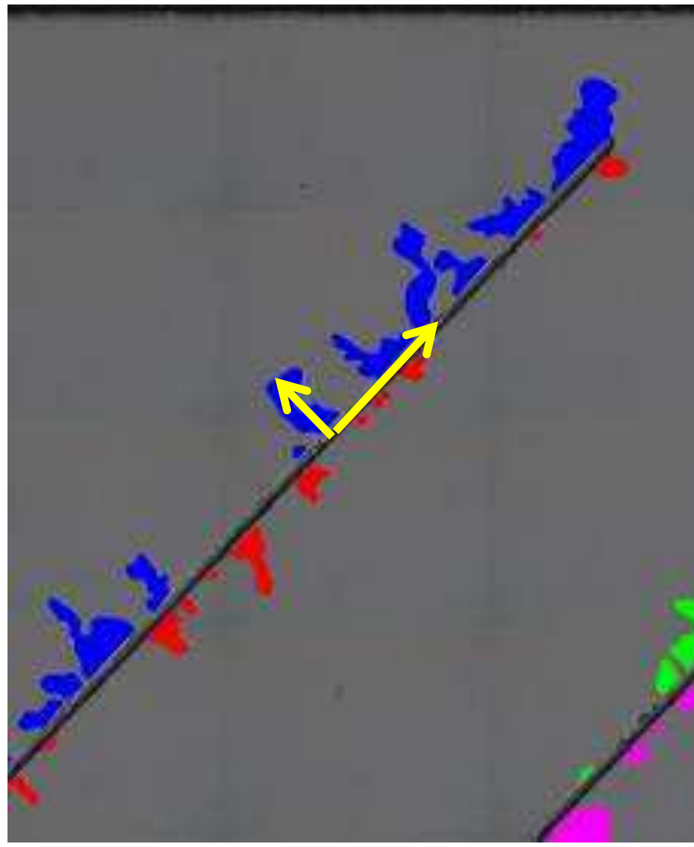
As exposed previously, the filiform corrosion can be seen as a two step process:

- The filament propagation process thought to be ruled by the differential oxygenation process can be modeled by the "i_couple" parameter.

- The initiation process thought to be ruled by corrosion of the substrate at the scratch.

This initiation step can influence the number of filaments starting but also how soon the filaments start, hence influencing as well the length of the filament after a given time.

- Two techniques were investigated to model the initiation by corrosion:
    - Resistance to polarization measurements
    - Electrochemical noise measurements



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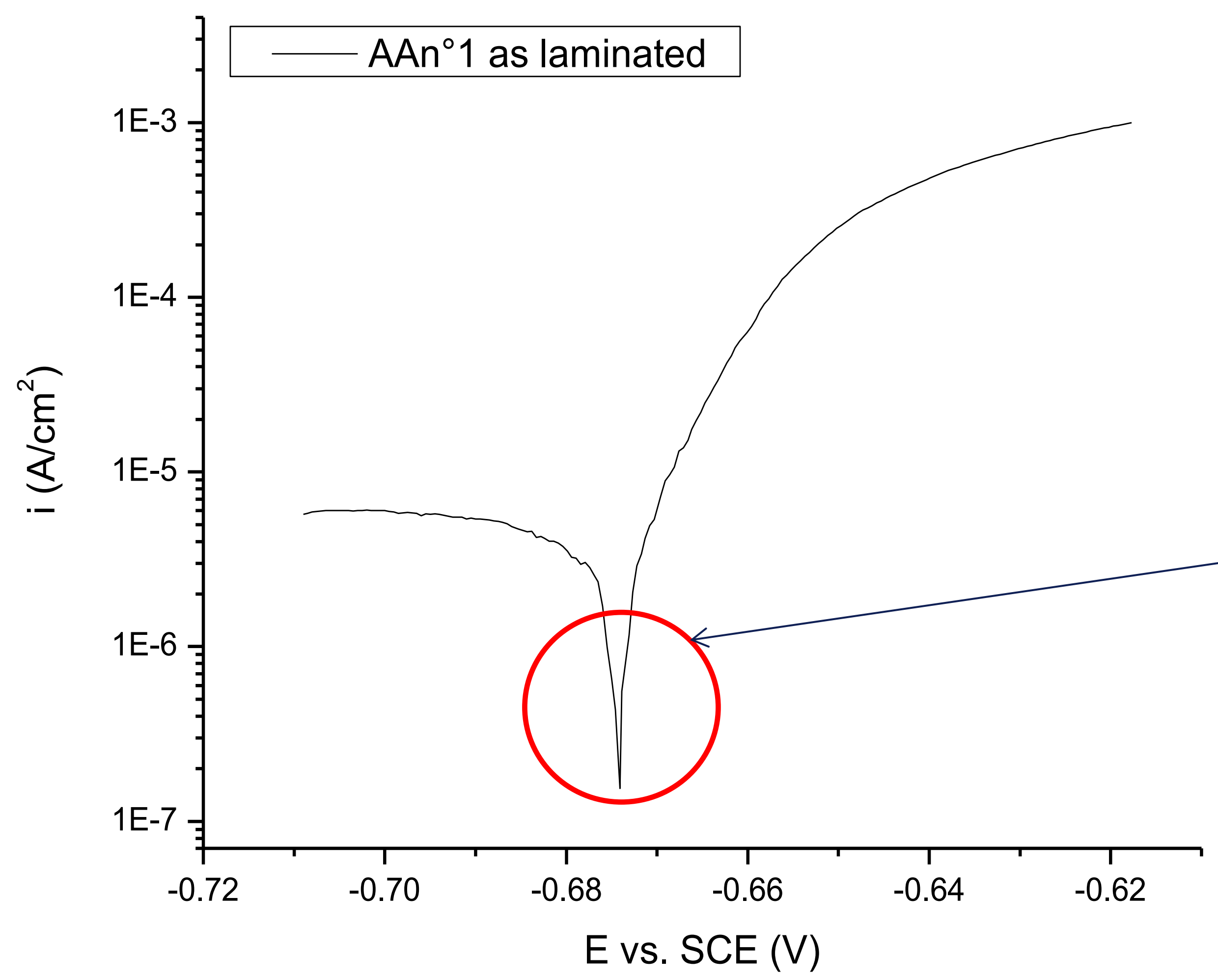
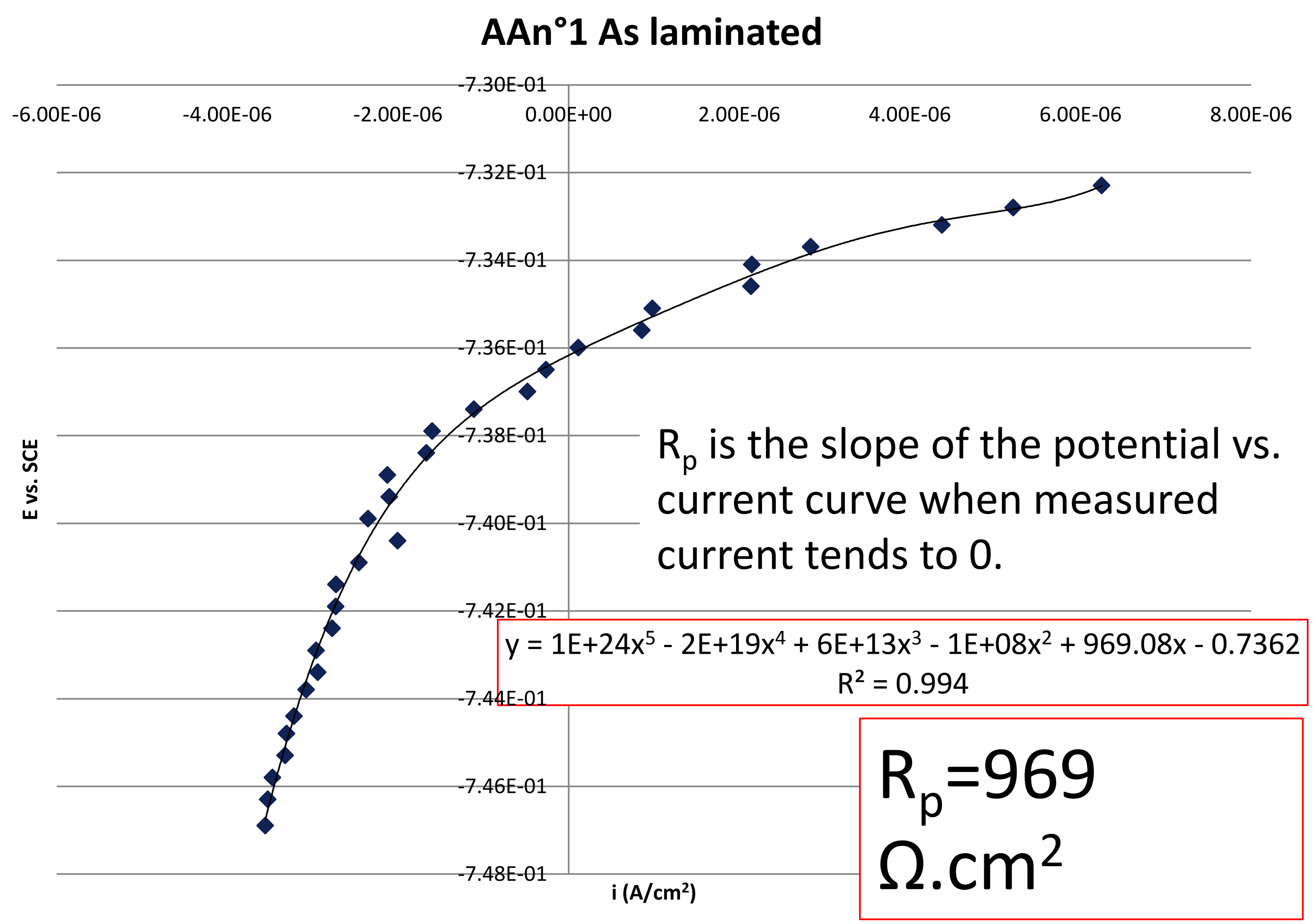
Phase 2: Electrochemical testing approach

› <u>Resistance to polarization</u> measurements to evaluate the susceptibility of substrates to <u>corrosion initiation</u>

- Resistance to polarization is inversely proportional to the corrosion rate => Higher is the resistance to polarization, lower is the corrosion current





R_p is the slope of the potential vs. current curve when measured current tends to 0.

R_p=969 $\Omega.cm^2$

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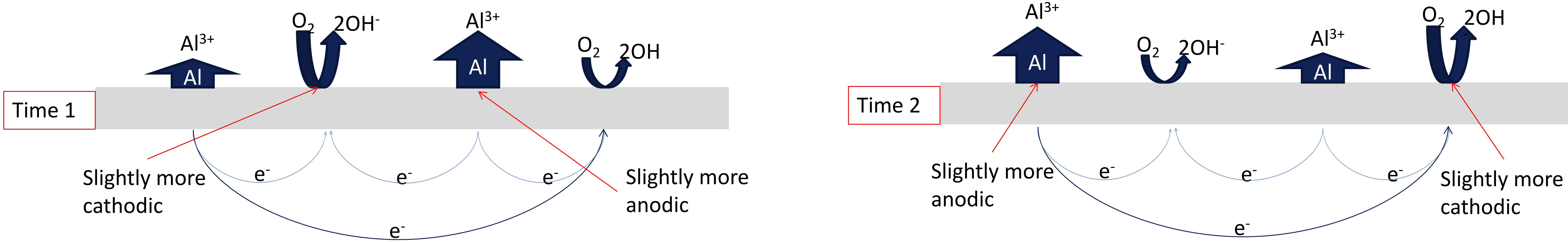
Phase 2: Electrochemical testing approach

› Electrochemical noise measurements to evaluate the susceptibility of substrates to corrosion initiation



Fluctuations due to statistically distributed corrosion process

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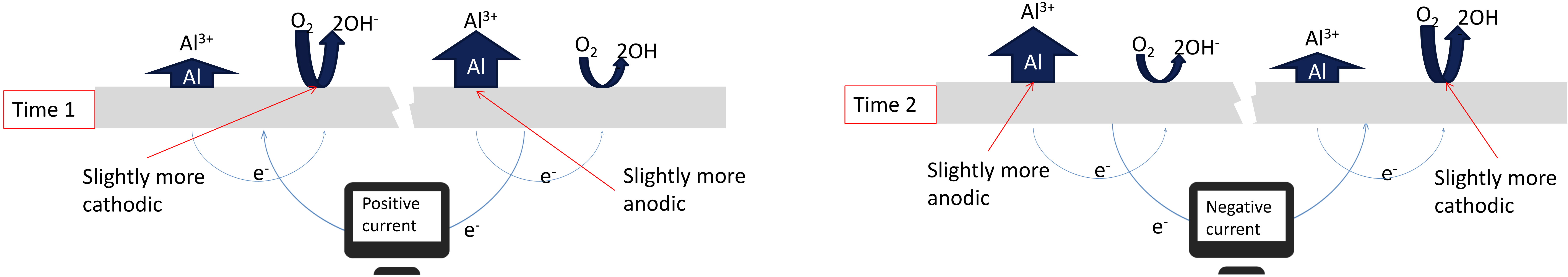
Phase 2: Electrochemical testing approach

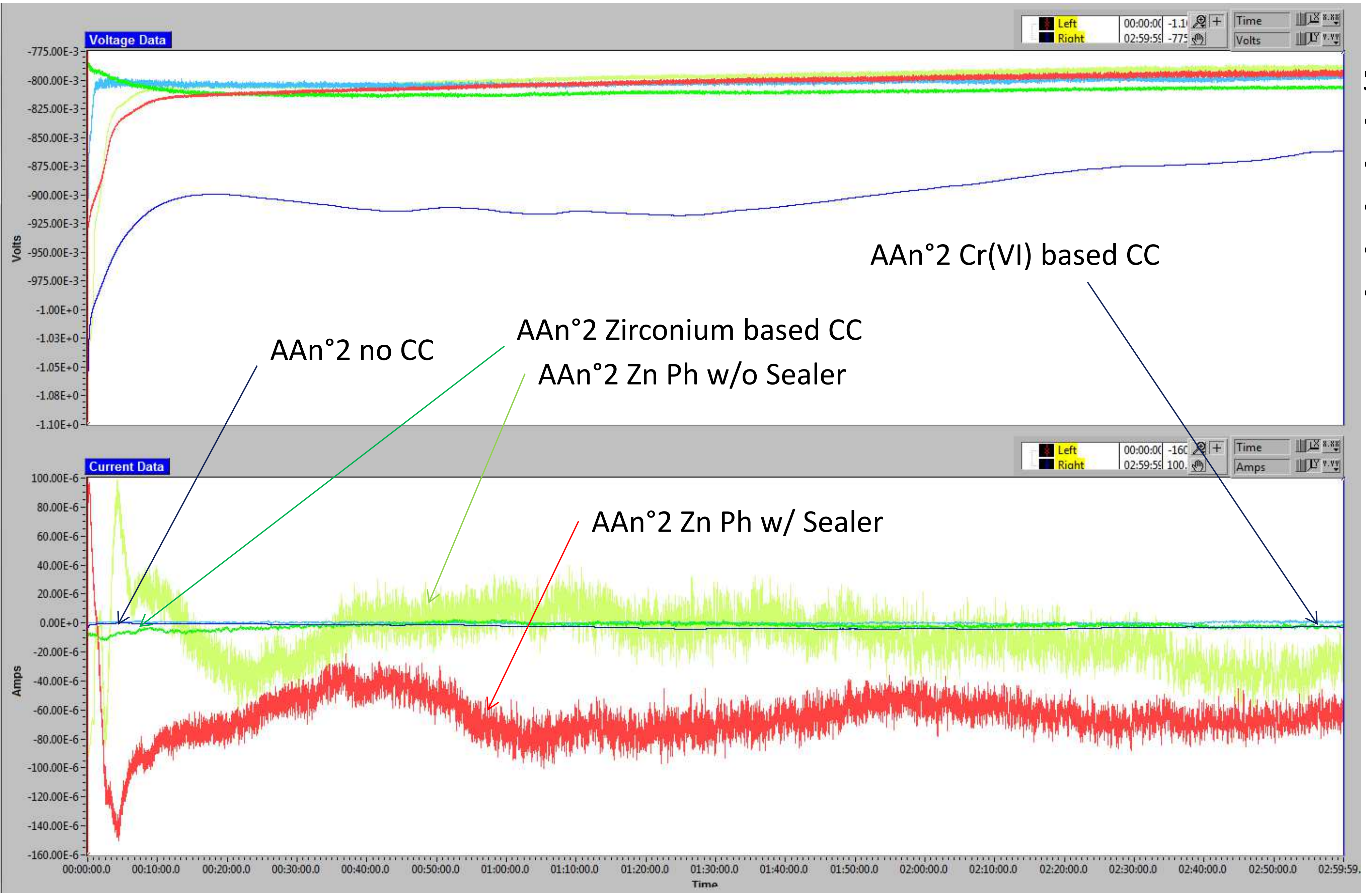
- Electrochemical noise measurements to evaluate the susceptibility of substrates to corrosion initiation



Fluctuations due to statistically distributed corrosion process

Phase 2: Electrochemical testing approach

› Electrochemical noise measurements to evaluate the susceptibility of substrates to corrosion initiation



Statistical analysis of the following parameters

- IRms = |Imean|
- σV : Voltage noise standard deviation
- σI : Current noise standard deviation
- Rn = σV/ σI : Noise resistance (same physical meaning as Rp)
- PI = σI / IRms : Pitting index (the higher it is the more localized corrosion is likely).

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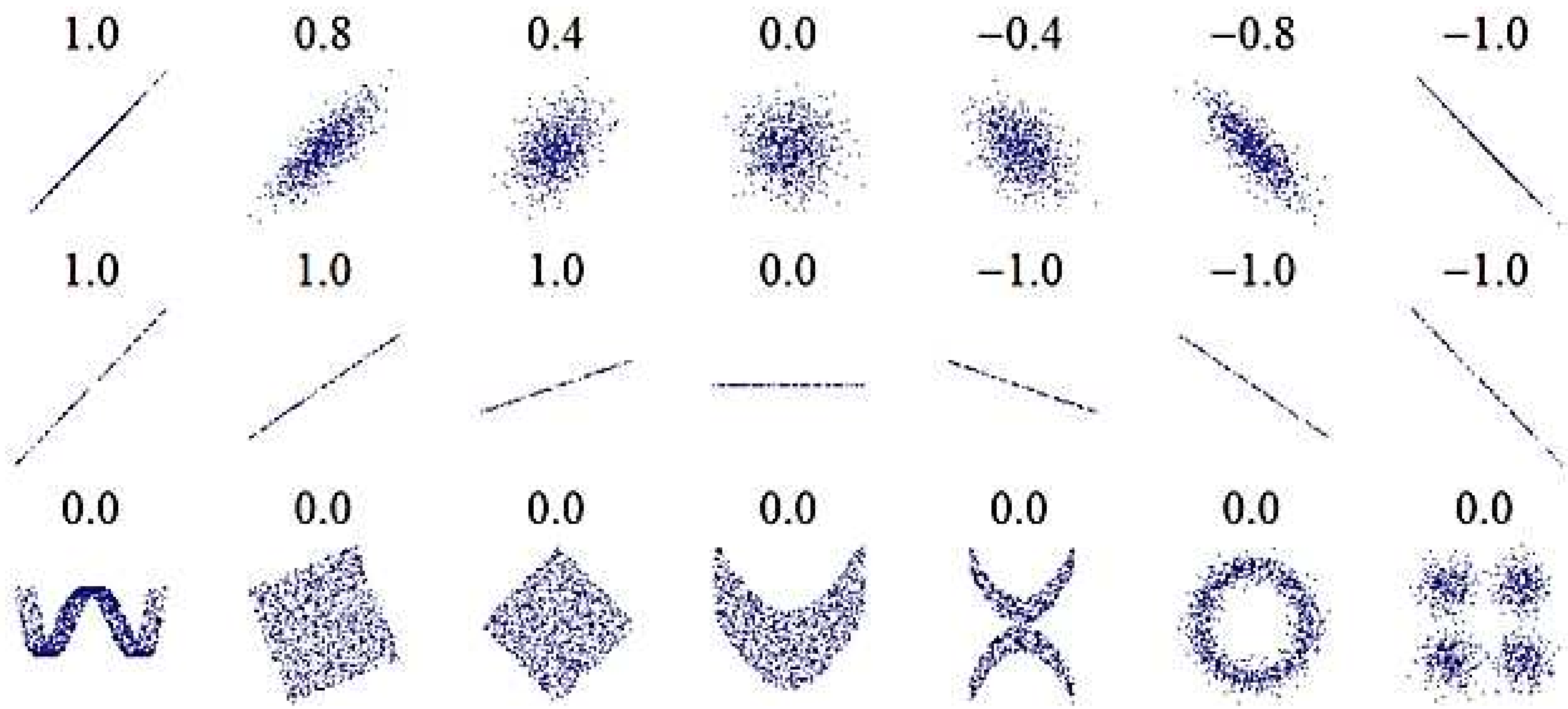
Phase 2: Electrochemical testing approach

Statistical analysis on mean values: Pearson correlation coefficient (a tool to explore data at a glance)

$$r = \frac{cov(X,Y)}{\sigma_x \sigma_y}$$

Suggested interpretation for r absolute value (Evans 1996):

- 0.00 - 0.19 : “very weak” correlation
- 0.20 - 0.39 : “weak” correlation
- 0.40 - 0.59 : “moderate” correlation
- 0.60 - 0.79 : “strong” correlation
- 0.80 - 1.00 : “very strong” correlation



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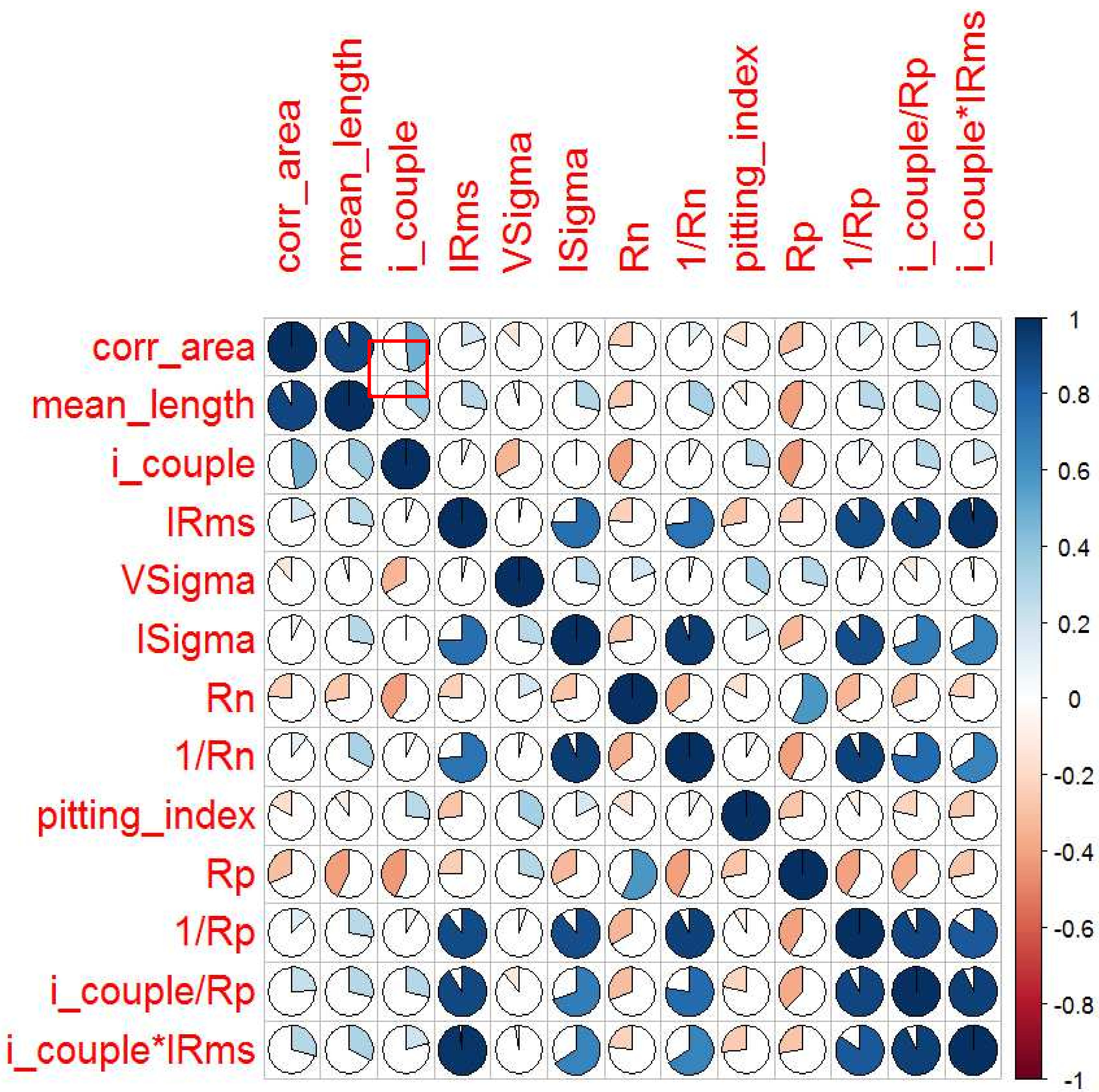
Statistical analysis on mean values: Pearson correlation coefficient

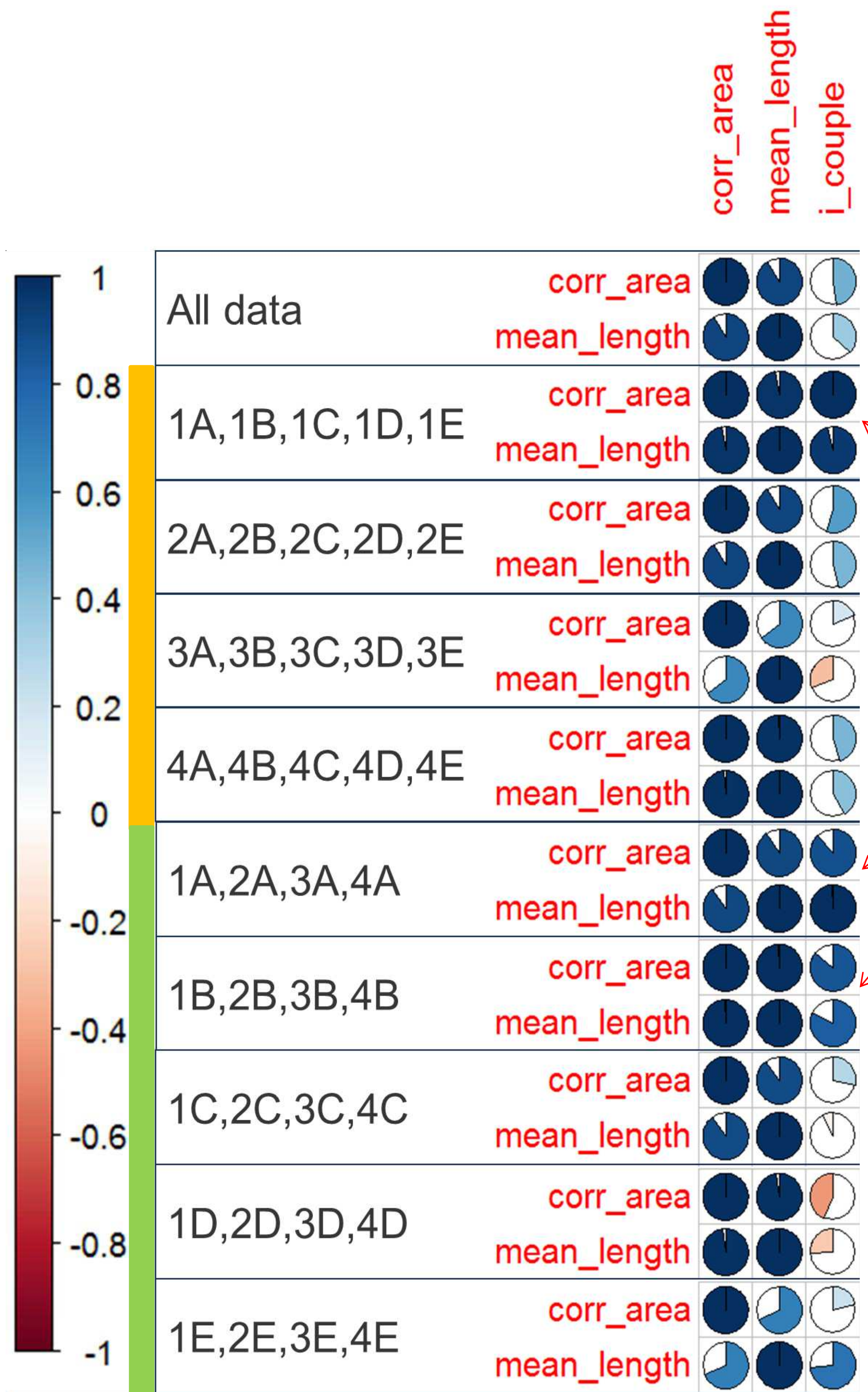


1	AAn°1 grinded
2	AAn°1 as laminated
3	AAn°2 as laminated
4	AAn°3 as laminated
A	No CC
B	Zn Ph w/ sealer
C	Zn Ph w/o sealer
D	Zr based
E	Cr based

When looking at all 20 AA/CC combination only moderate correlation observed between i_couple and corr_area

i_couple is a parameter designed to firstly correlate mean_length before corr_area. i_couple should not correlate corr_area better than mean_length. This means that the moderate correlation observed with corr_area has no physical sense when looking at all the data.

Statistical analysis on mean values: Pearson correlation coefficient



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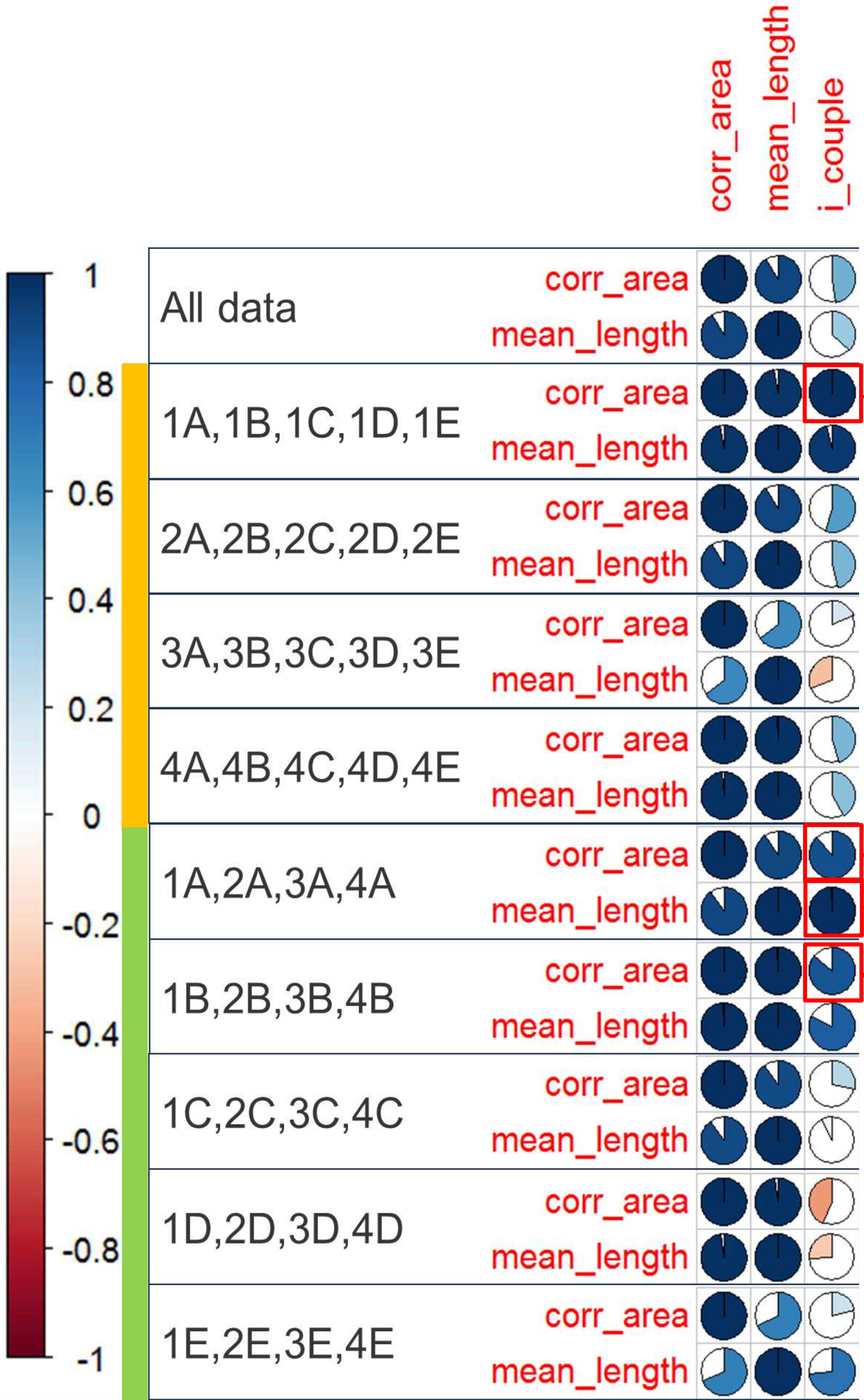
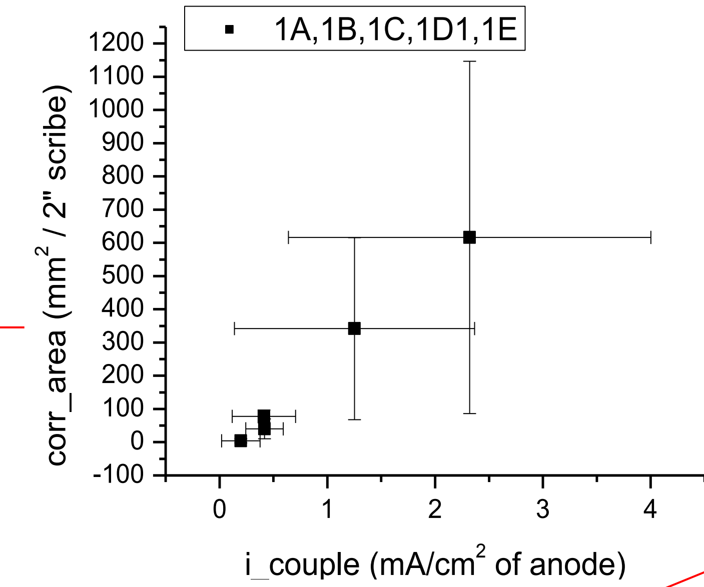
When looking at subsets of data, very strong correlations of i_couple with mean_length and corr_area are observed for:

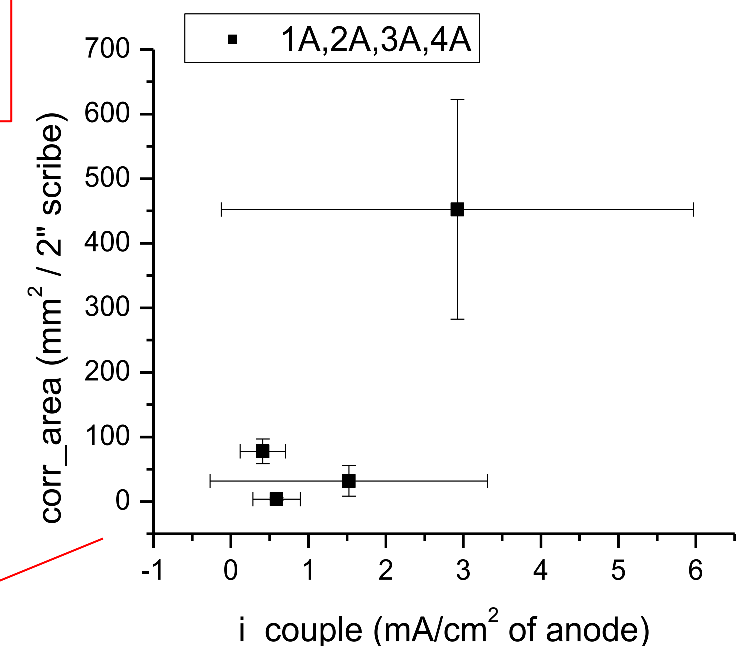
- samples with no conversion coating
- samples with Zn Phosphate + sealer CC
- samples prepared with grinded AAn°1

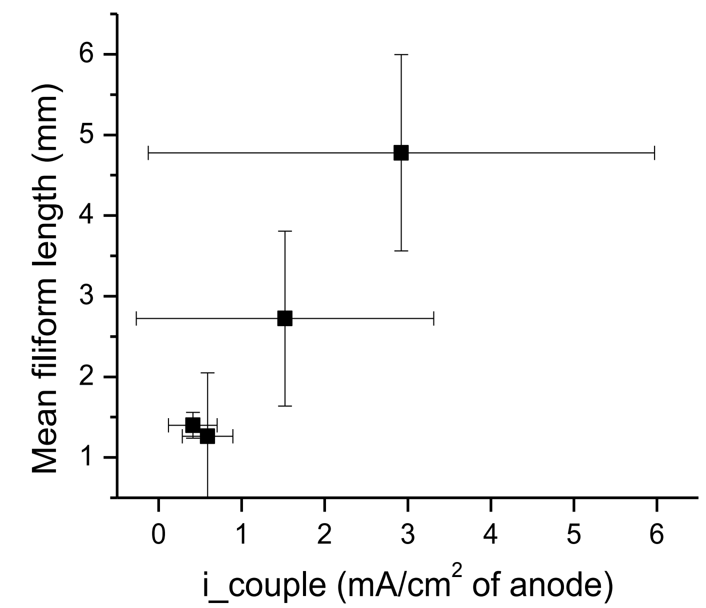
Statistical analysis on mean values: Pearson correlation coefficient

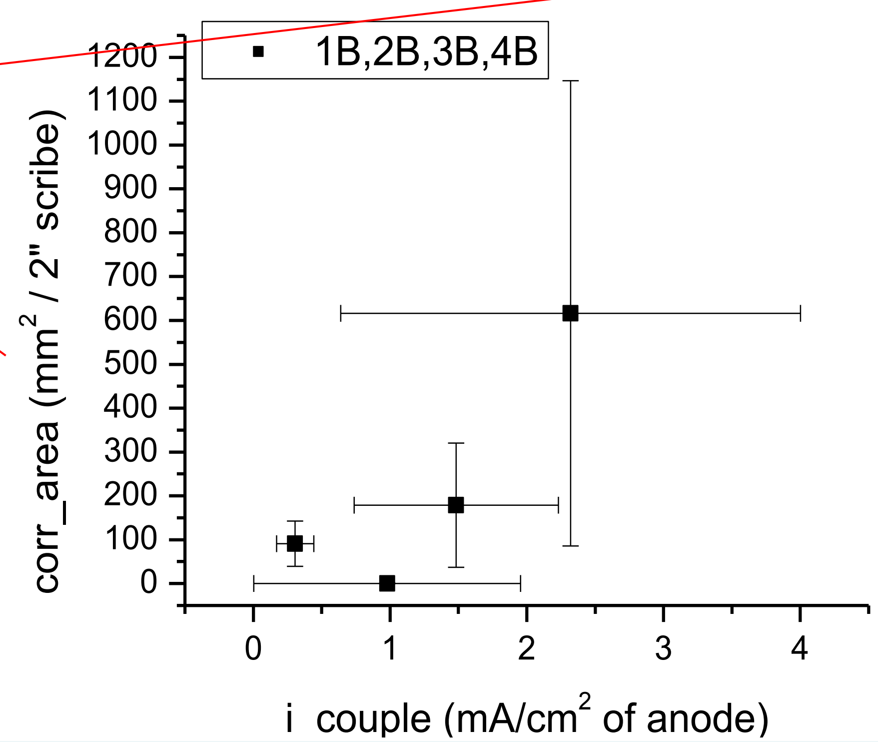


Very good correlation between “i_couple” and “corr_area” suggests that grinded AAn°1 is highly susceptible to the propagation process.









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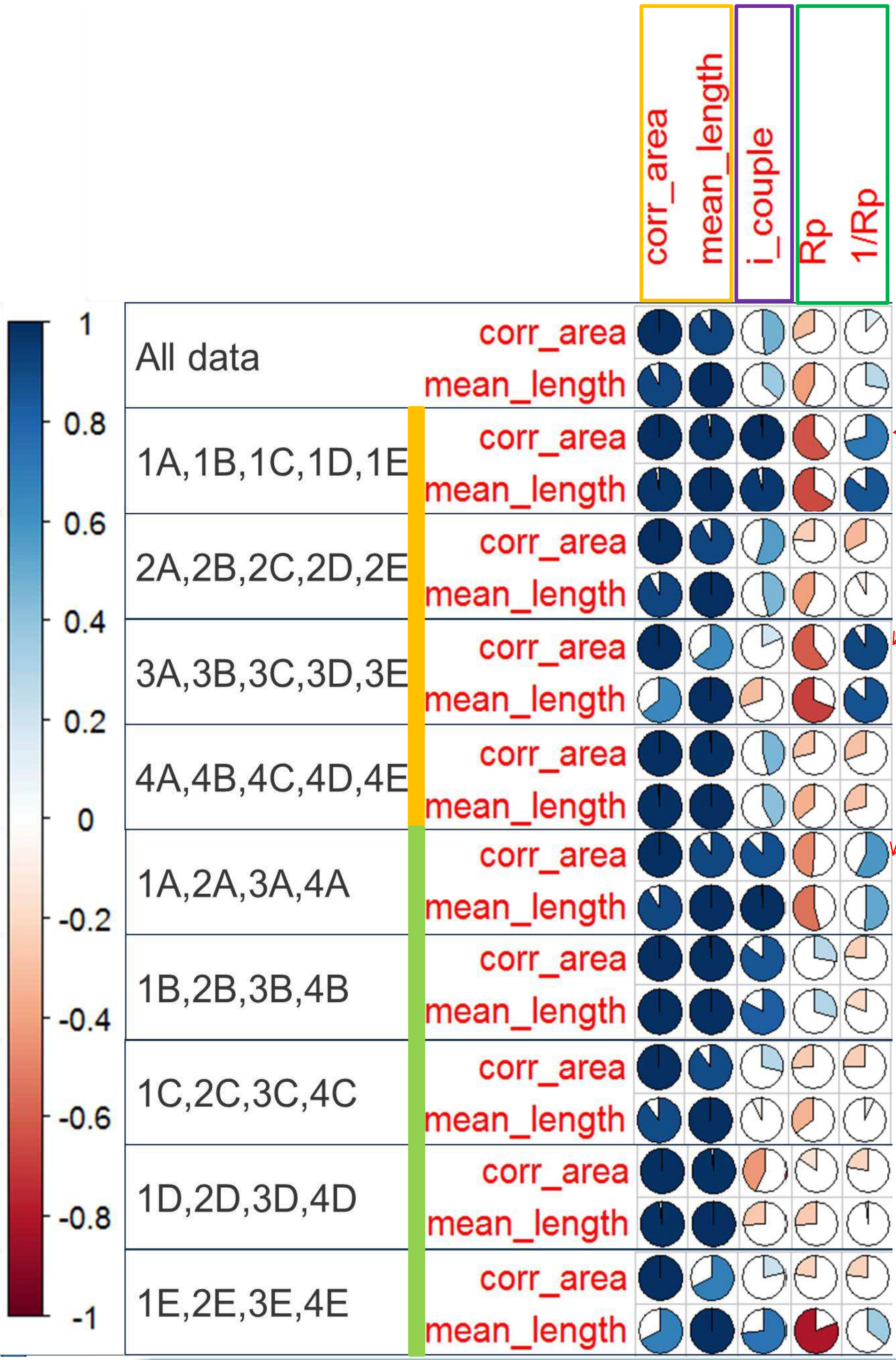
Statistical analysis on mean values: Pearson correlation coefficient



R_p seams to play a role in the susceptibility to filiform corrosion of some subsets only.

AAn°2 samples: 1/Rp shows a strong correlation with the corrosion extent observed on the painted samples. This suggests that the susceptibility to filiform corrosion of these samples is mainly depend on the initiation step.

1	AAn°1 grinded
2	AAn°1 as laminated
3	AAn°2 as laminated
4	AAn°3 as laminated
A	No CC
B	Zn Ph w/ sealer
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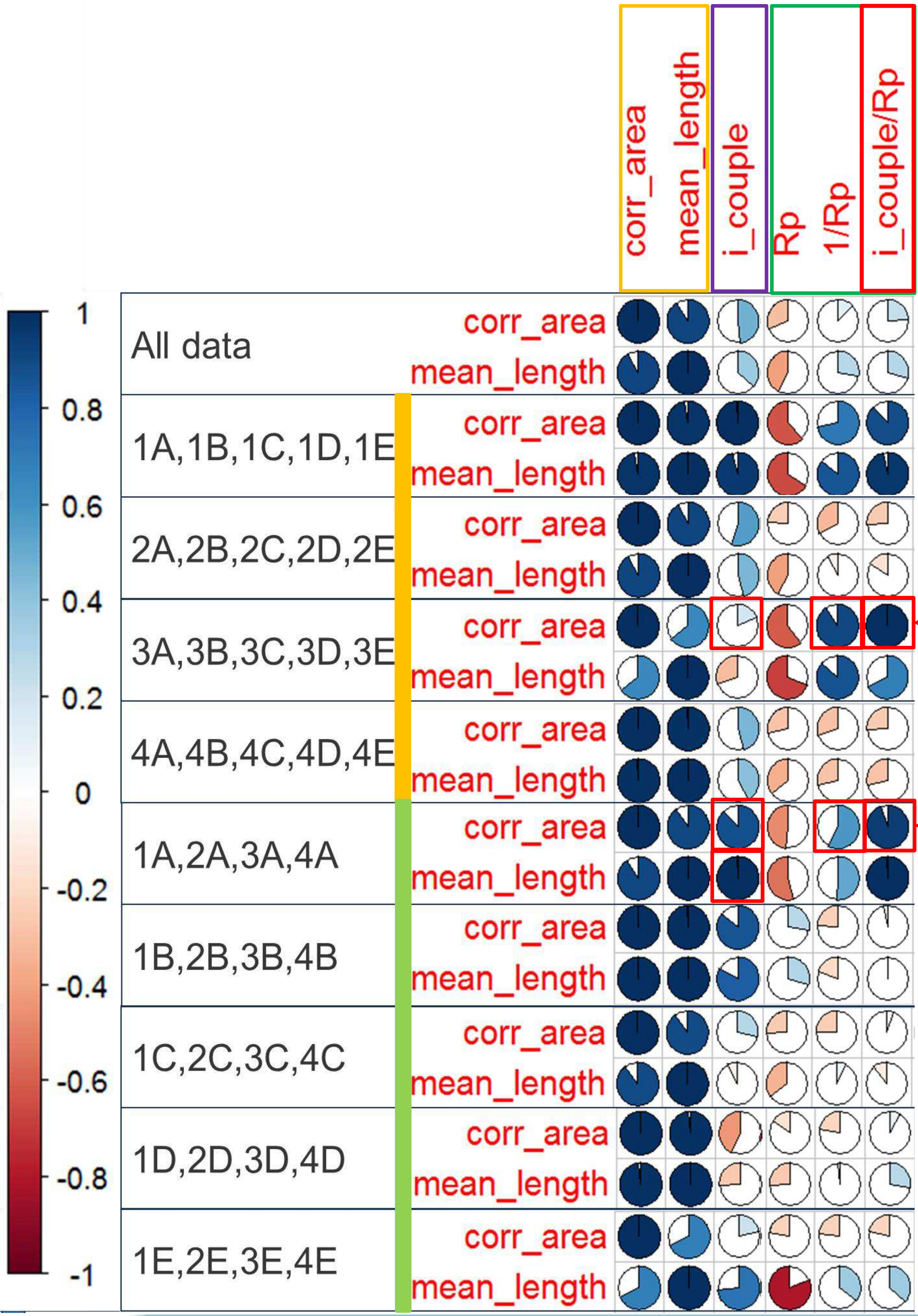
Statistical analysis on mean values: Pearson correlation coefficient



A two steps process means that there should be a combined effect of the two parameters:

- if a sample “x” is very susceptible to the propagation phenomenon but very resistant to the initiation corrosion, this one will show few filaments but these will be long,
- if a sample “y” is susceptible to corrosion (low Rp value), but the propagation phenomenon is not what’s driving the corrosion, the corrosion will present either no corrosion, or many filaments but small in length,
- If a sample “z” is susceptible to both type of corrosion, this one will show many long filaments.

While R_p seamed to correlate quite well the corrosion extent, taking into account i_couple increases the correlation factor.

Combined effect seams to be also observed in the case of samples without conversion coatings.

1	AAn°1 grinded
2	AAn°1 as laminated
3	AAn°2 as laminated
4	AAn°3 as laminated
A	No CC
B	Zn Ph w/ sealer
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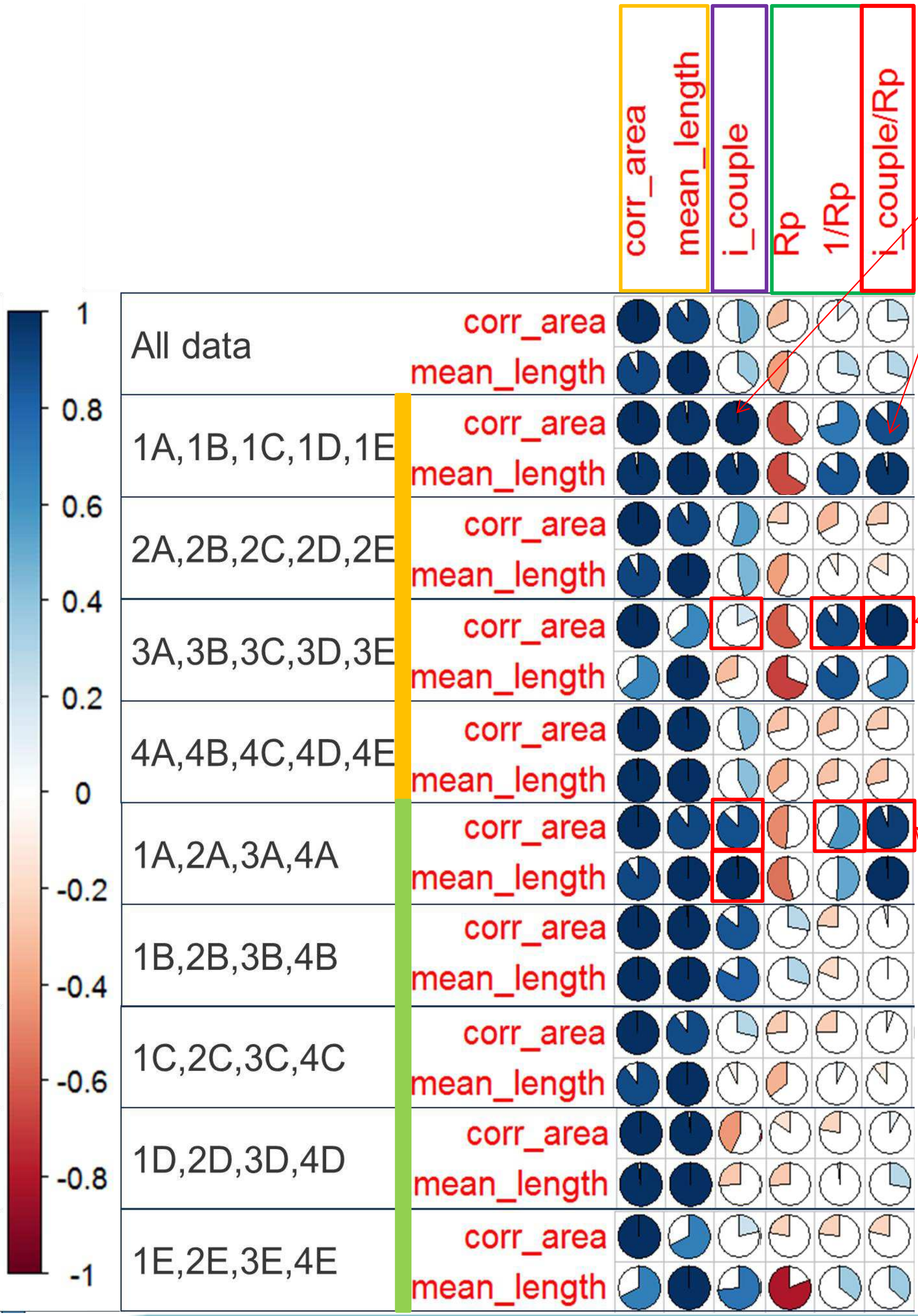
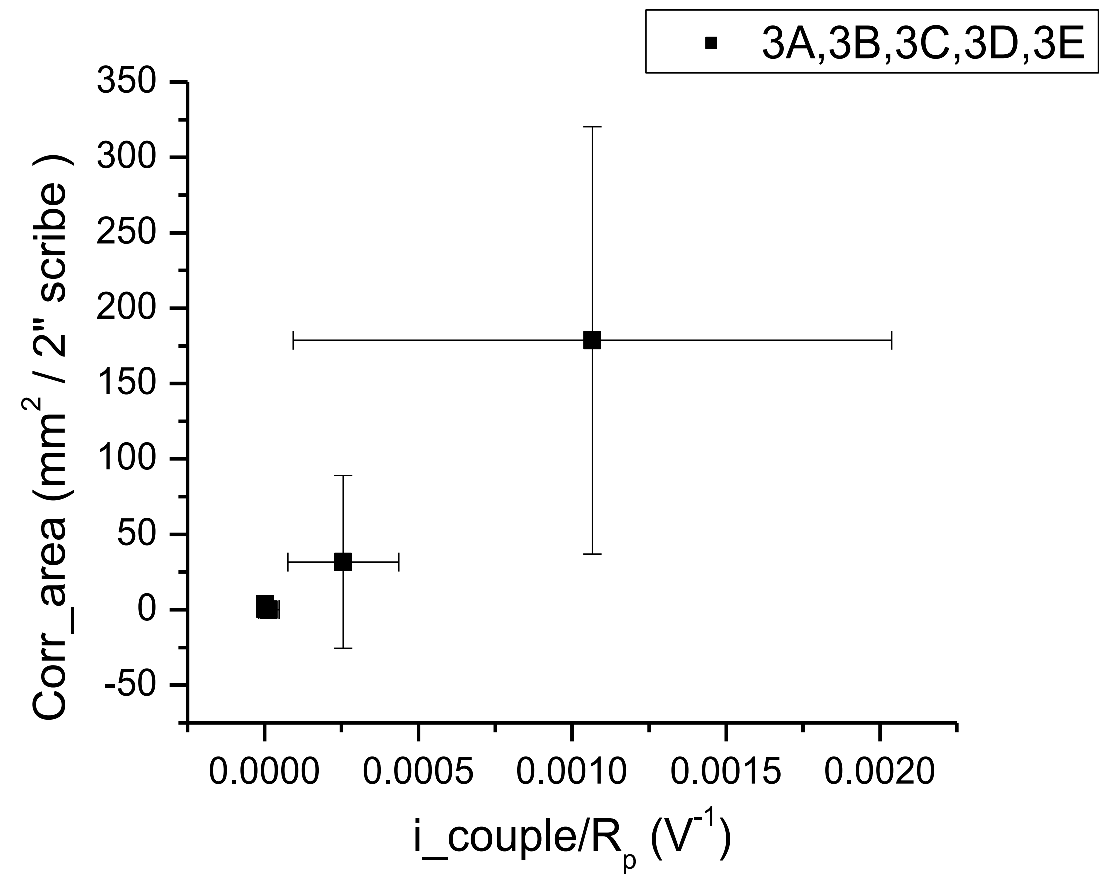
E	Cr based

Statistical analysis on mean values: Pearson correlation coefficient



Looking at i_couple/Rp is detrimental in the case of AAn°1 grinded



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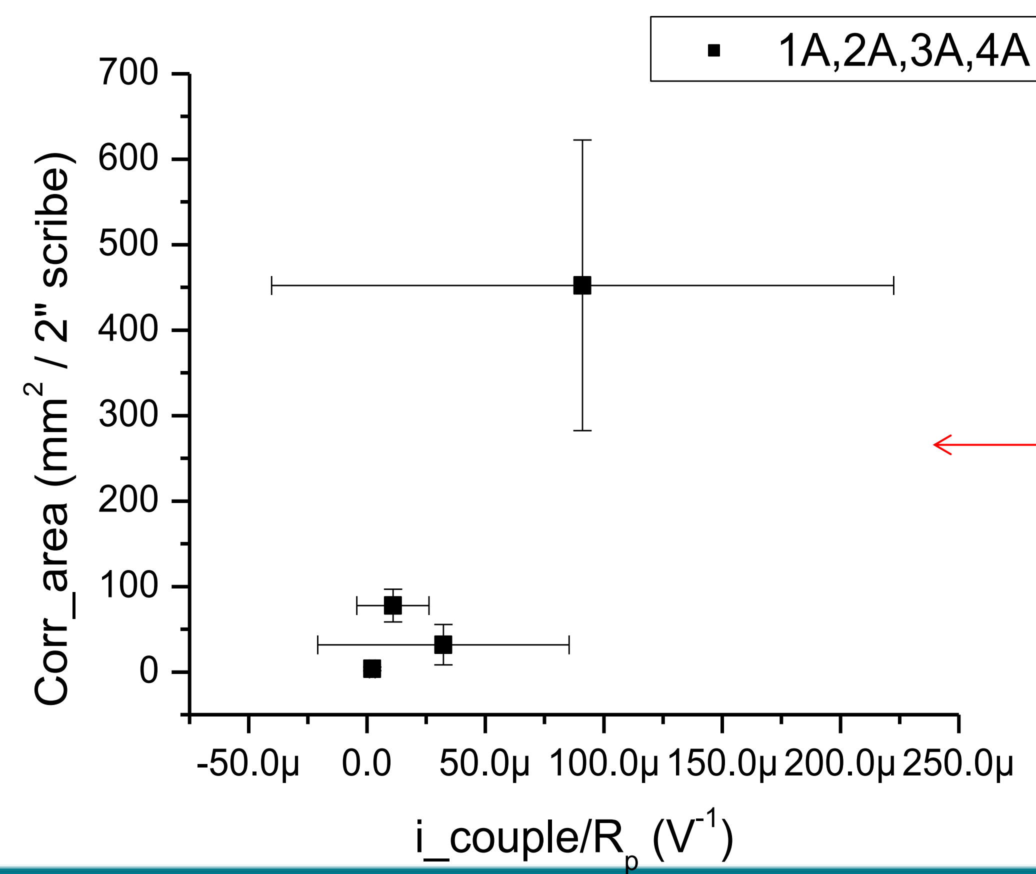

More points are needed to confirm the relationship

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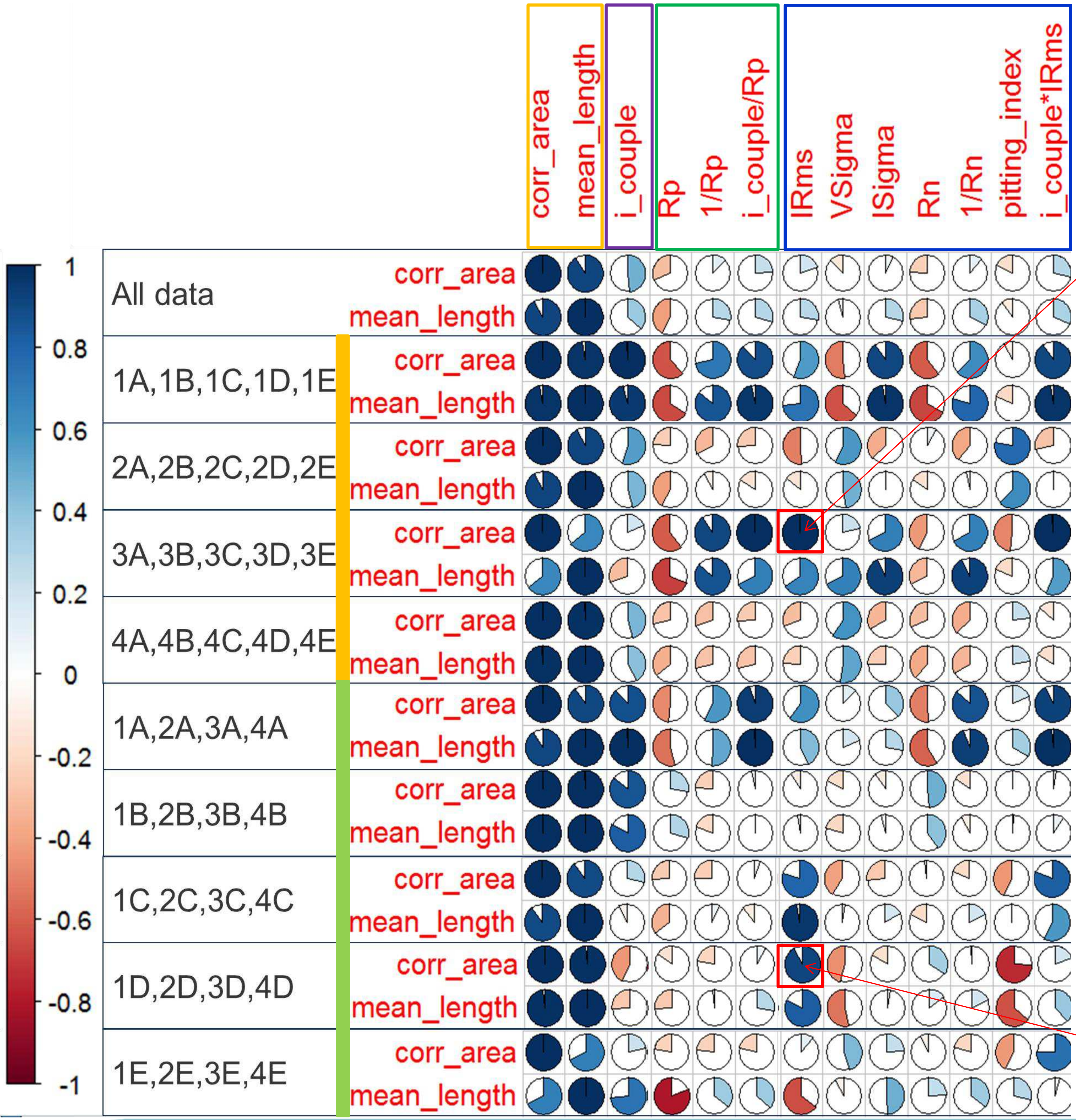
Statistical analysis on mean values: Pearson correlation coefficient



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A	No CC
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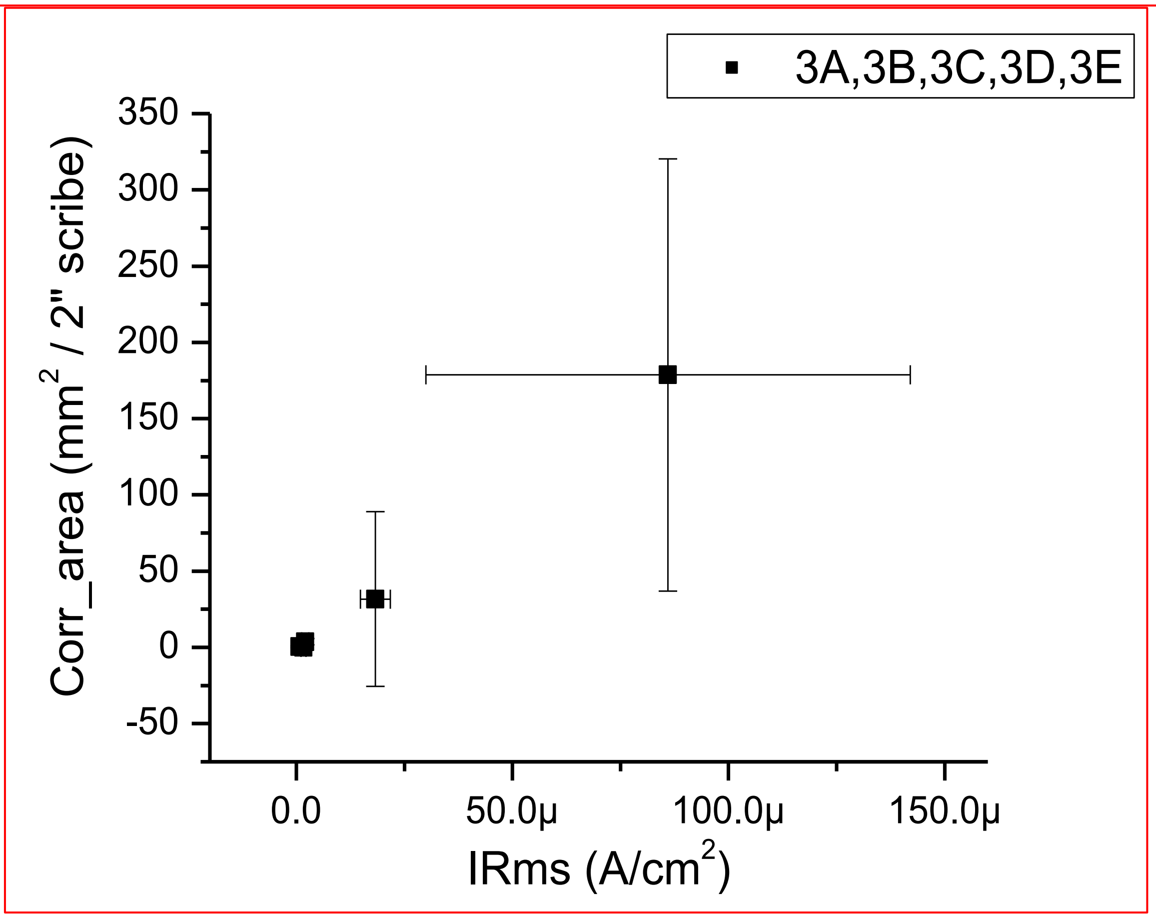
D	Zr based
E	Cr based

AAn°2: Very good correlation between "IRms" and "corr_area", confirming once more the influence of the initiation process on the samples susceptibility to filiform corrosion.



Zr based CC: good correlation is found between "IRms" and "corr_area", suggesting that the main protection mechanism provided by the CC is through protection against general corrosion.

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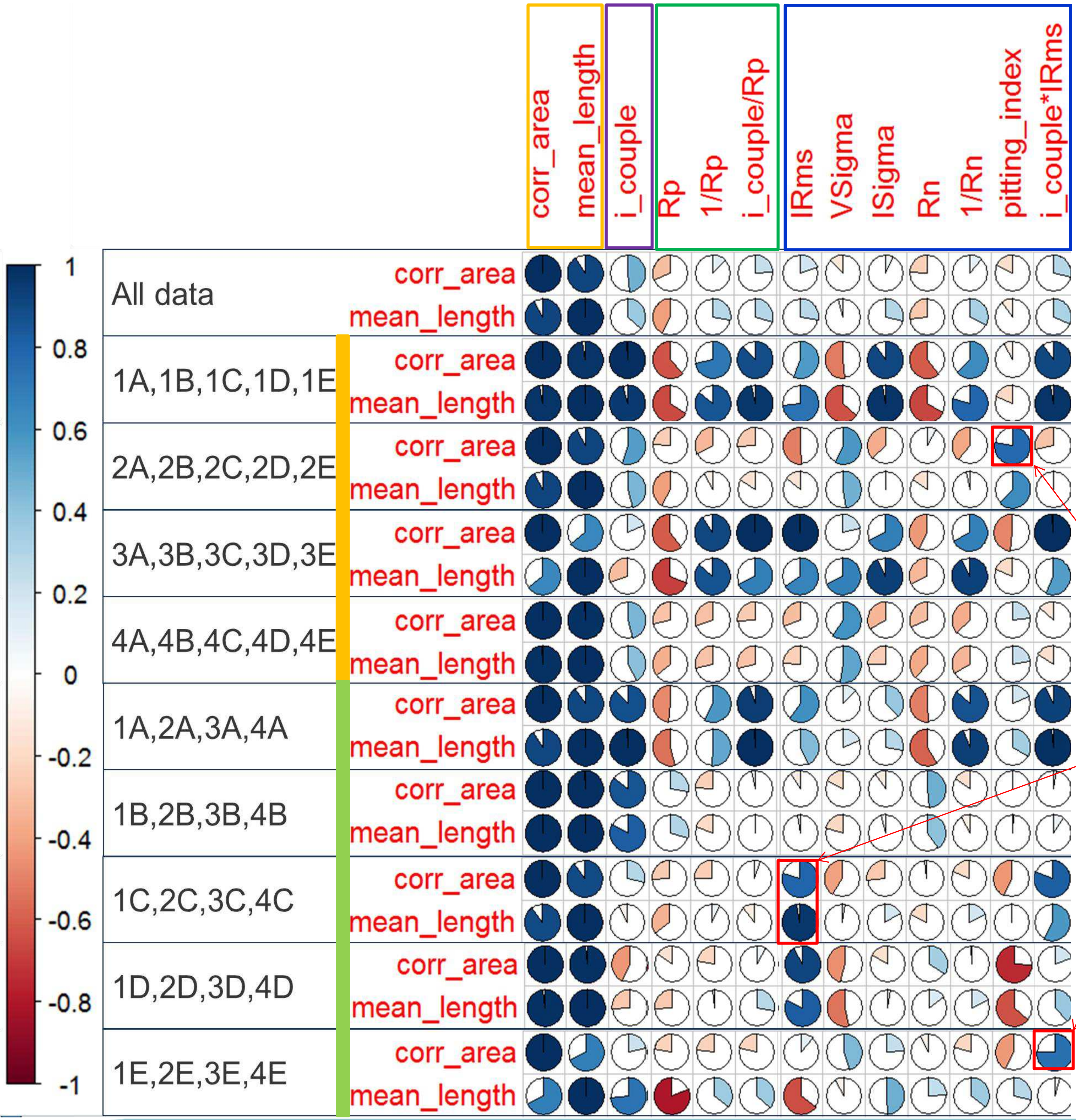
Statistical analysis on mean values: Pearson correlation coefficient



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Other correlation trends up to now not found with other parameters

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Phase 2: Electrochemical testing approach

- When looking at the all whole test matrix involving different alloys and different conversion coating, no correlation was found between the selected electrochemical parameters and the corrosion observed.
- However, when keeping either the aluminum alloy or the CC as a constant, correlations arise:
  - "IRms" correlates perfectly the mean corroded area observed for the AAn°2 samples.
    - It would be interesting to confirm the trend with various alloys of the series.
  - "i_couple" correlates the mean length of filaments observed for samples prepared without conversion coating, and the "i_couple/R_p" correlates quite well the mean corroded area.
    - If confirmed with more alloys, this could potentially be a tool for the alloy developers.
  - "i_couple" correlates the corroded area observed for the grinded AAn°1.
    - If this trend was to be confirmed with other grinded alloys, this could be a selection tool to evaluate the worst case scenario as it is recognized that corrosion filiform is more important in places where alterations were done (repairs, machining…).
- As a general rule, each correlations observed should be confirmed with more data points

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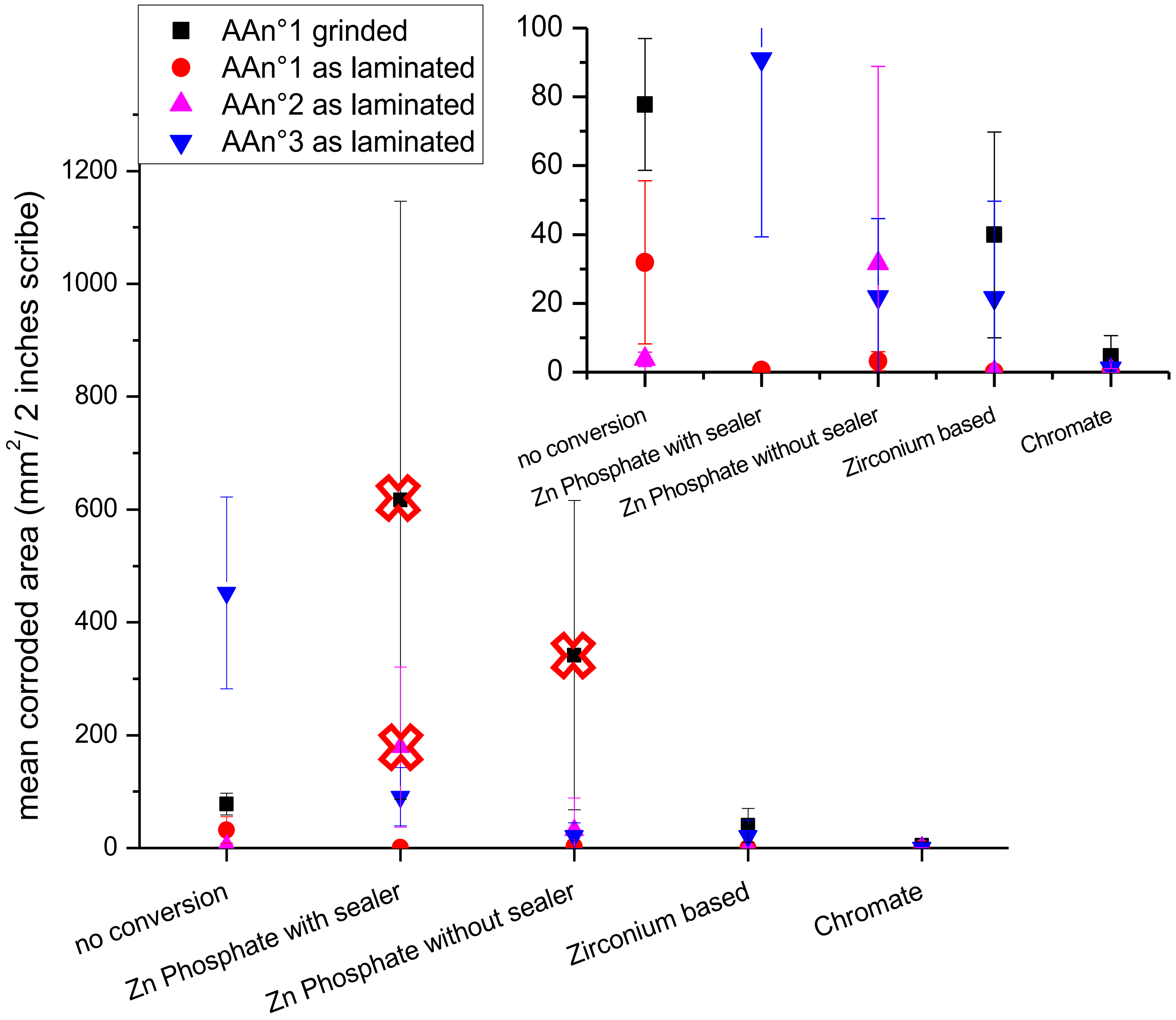
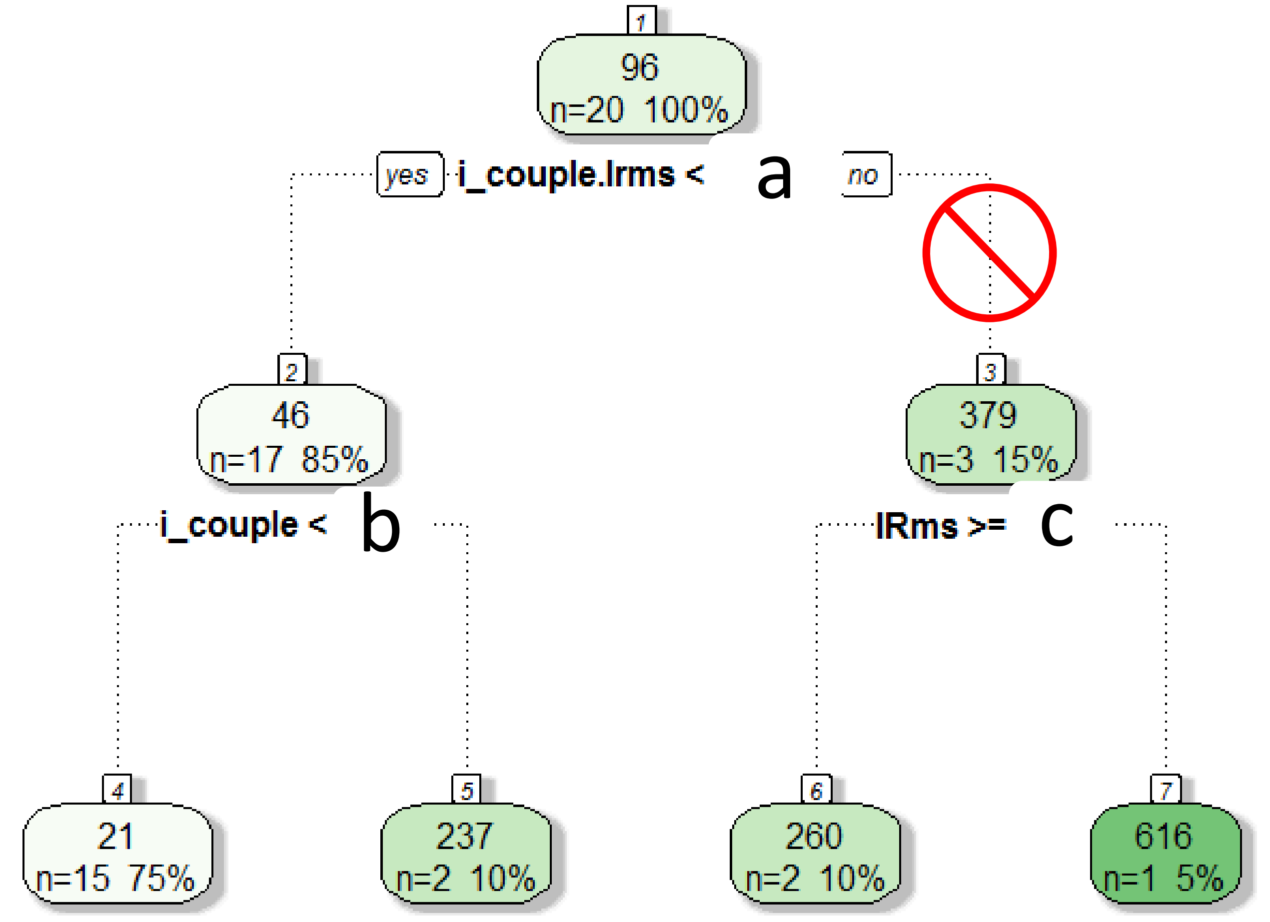
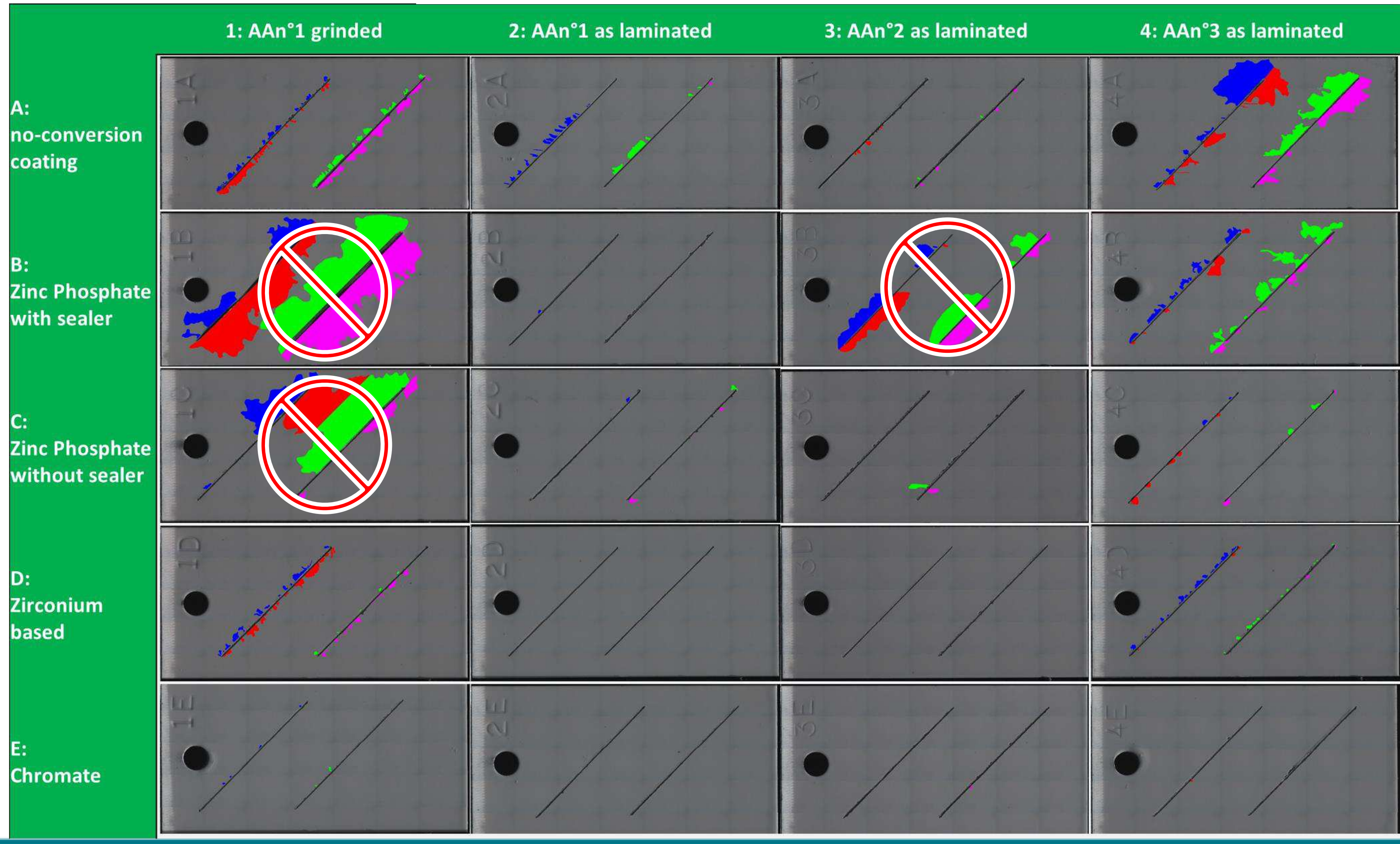
Defining threshold values

- For such a wide span test matrix, can we define threshold values in order to rule out the most at risk Alloy/CC combinations at an early stage of the selecting process and that way reduce the number of combination to paint and test in environmental chamber?
  - Can we find parameters for which the value is systematically high (or low) when corr_area is high?
  - Through “Rattle” package in R software, one can generate different decision trees.
    - Considering the small amount of data points (20 average values per parameters) all data was used to built and train these decision trees.

Defining threshold values

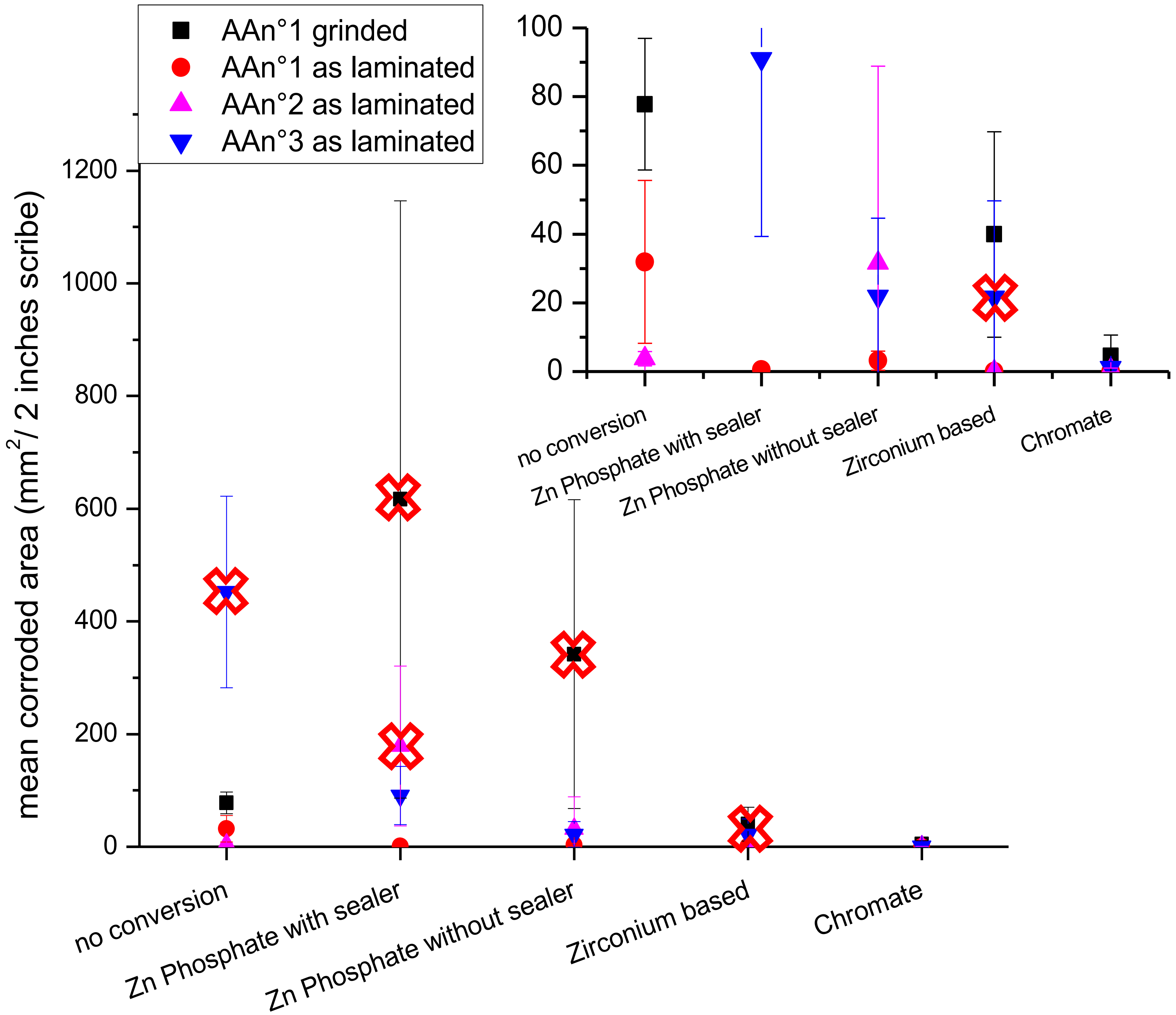


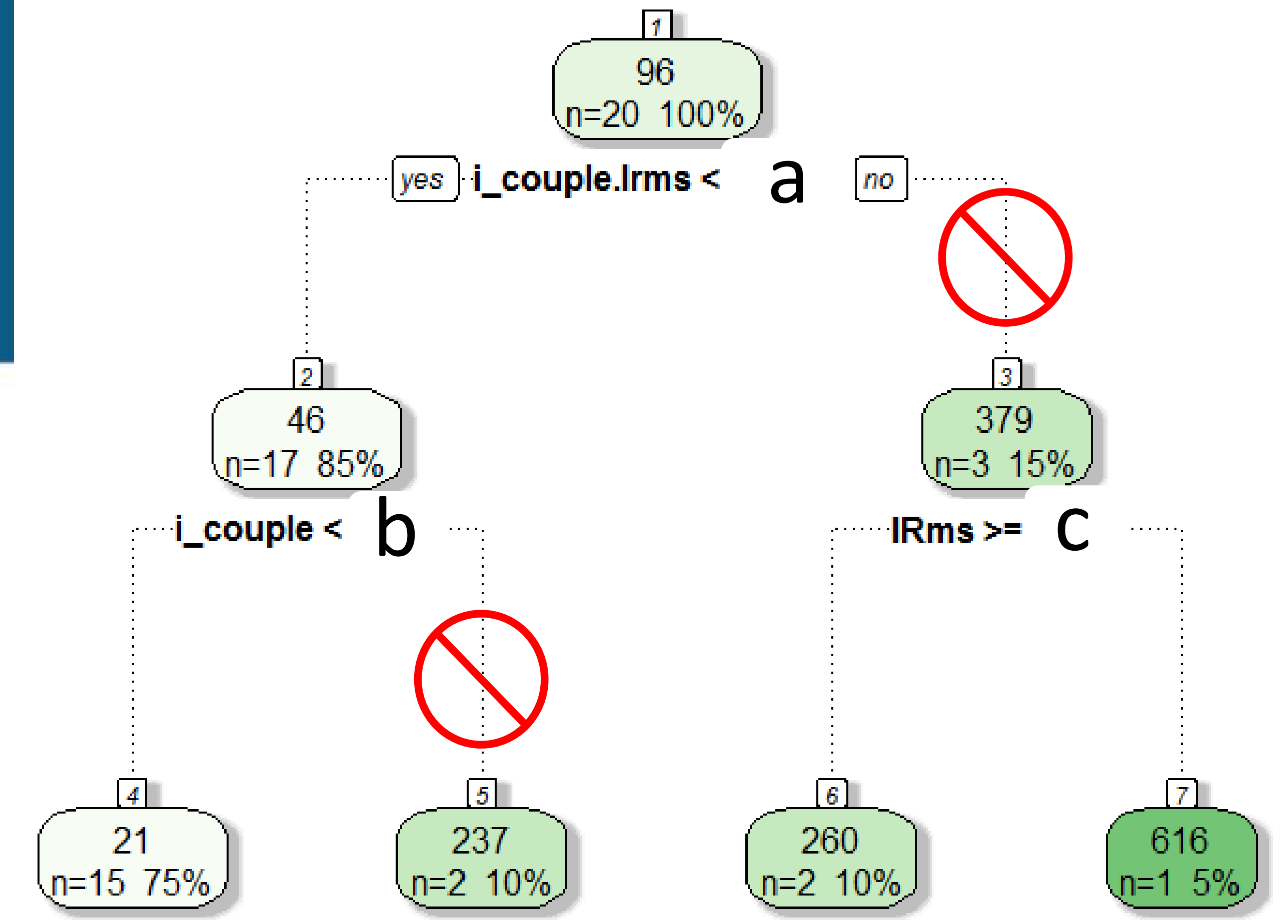


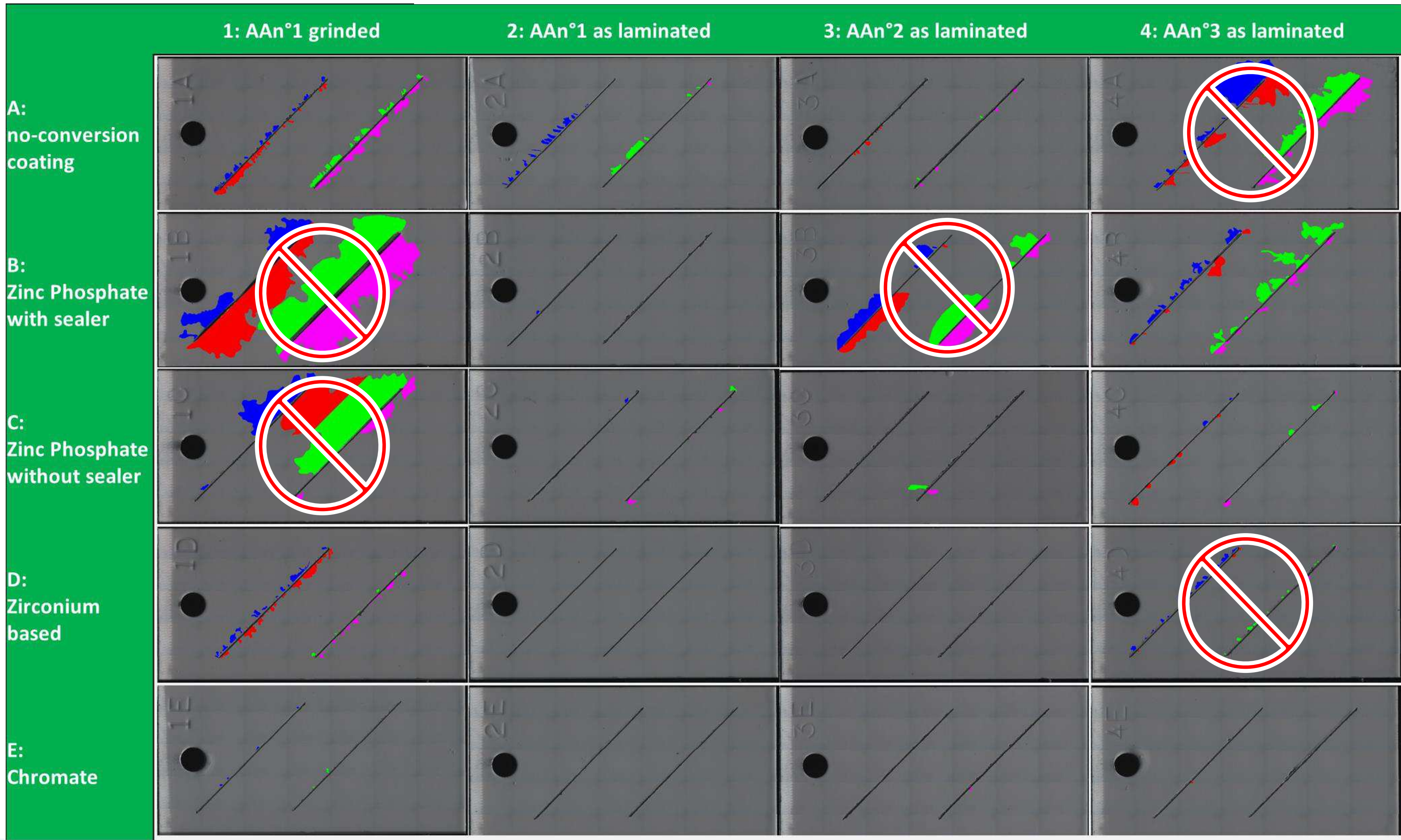


NRC·CNRC

Defining threshold values







NRC·CNRC

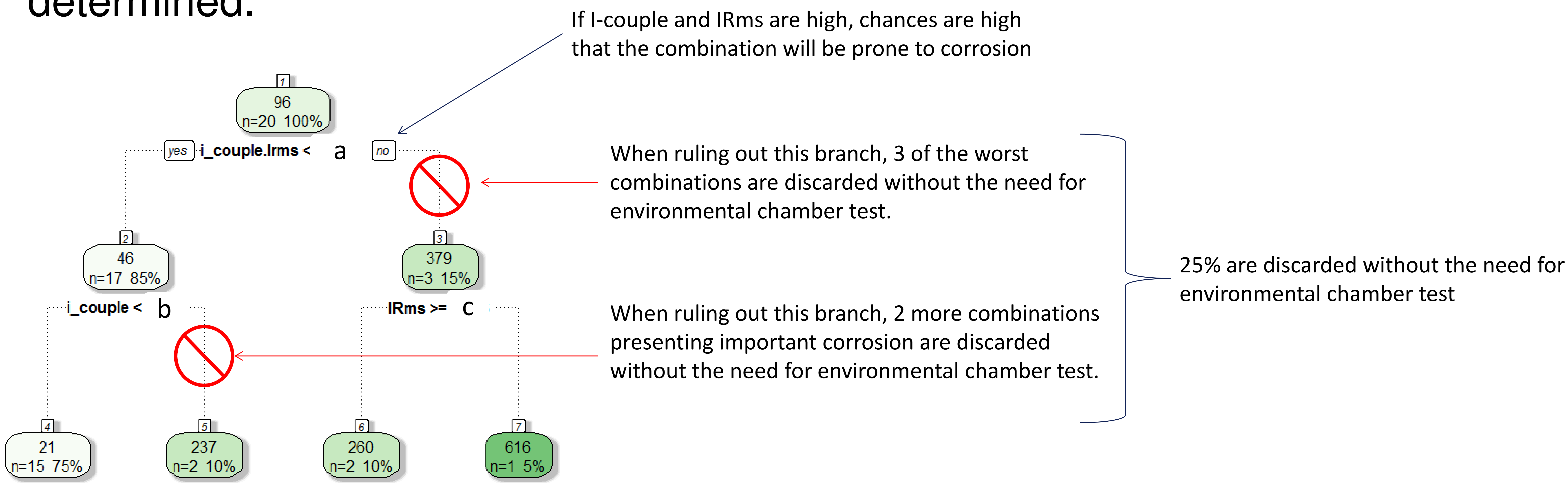
Summary

- When considering subsets, correlations were found between electrochemical parameters and the corrosion observed after the standard laboratory test

- This electrochemical approach showed to be promising when studying test matrix with limited changes in variables (constant CC or constant alloy).
  - Hence it could potentially find its application in:
    - developing aluminum alloy composition resistant to filiform corrosion
    - selecting conversion coating for a set alloy (seams especially suitable for AAn°2 series)

Summary

- Looking at decision trees built to predict the corroded area for all 20 combinations, threshold values for some electrochemical parameters were determined.



Considering the small amount of data points (20 average values per parameters) all data was used to built and train the decision tree. More data point would be needed to test and confirm the tree (especially to confirm that the branch 5 can be ruled out without the risk of discarding valuable options).

NRC·CNRC

Thank you for your attention!

Any questions?

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