

NEW Cr-FREE SEALING TEST LNEC STUDIES

Phosphoric acid immersion test for the assessment by mass loss of the
anodic oxide coating sealing quality

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Previous studies on CPA (ISO 3210) alternative sealing tests



➤ 2011/2012 LNEC studies

Different acid test solutions

- Sulphuric acid (38°C, 50°C)
- Acetic acid and sodium acetate (at boiling point)
- Phosphoric acid (38°C)

Phosphoric acid (PA)
immersion test as the
best alternative

Application to different sealing processes

- Hot water
- Mid-temperature (Ni-free)
- Cold sealing

➤ 2011 QUALANOD RRT

Comparison PA and CPA mass loss test methods

CPA mass loss test ($m < 30 \text{ mg.dm}^2$)

- Repeatability=1,1
- Reproducibility=2,3

PA vs CPA
similar response

PA mass loss test ($m < 30 \text{ mg.dm}^2$)

- Repeatability=1,5
- Reproducibility=3,6

Proposal of PA new standard to ISO/TC 79/SC 2

Berlin (5-10-2012)

Based on ISO 3210 – Method 2 (CPA) procedure, without Cr oxide

- **Limitation:** presence of uncoated surfaces contribution to mass loss of aluminium dissolution

Italia and China also presented PA tests results . China show PA tests results carried out on partially anodized specimens showing with significant influence of aluminium bare surfaces

ISO DECISION: A new task allocated to ISO/TC 79/SC 2/WG 15

Further evaluation of the PA test should be carried out on influence of uncoated surfaces

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CPA replacement by PA test

Two main aspects raise concern:

- Bare aluminium influence.
- Mass losses differences variability between PA and CPA tests.

2013 LNEC STUDIES

Study 1: *LNEC extend research on PA test to address the question of aluminium dissolution and test conditions*

Obj 1: Influence of tests conditions

different acid concentration and temperature of test solution, and different immersion time were tested

Obj 2: Influence of method used to remove the anodic coating and % of uncoated surface on aluminium attack
chemical etching, mechanical abrasion.

Study 2: *QUALANOD included in Inspections PA test in parallel with CPA
to evaluate PA results on real plant situations*

Study 3: *2013 QUALANOD RRT also included PA test*

- Different sealing conditions, solid and hollow test specimens

Study 1

Objective 1 : Bare aluminium influence

Phosphoric acid, in the absence of chromium (VI), attacks aluminium.

- In what extent this affects mass loss values?
- Can this dissolution be predictable?
- There is a maximum uncoated area limit above which the PA mass loss test becomes unfeasible?
- Needs to mask the uncoated zones

Study 1

OBJ2: PA test results variability

Mass loss differences between PA and CPA tests show some variability

- What is the cause?
- Is possible to establish a maximum mass loss acceptance limit as there is for the CPA test?

Study 1

Impact of PA test conditions on Al attack

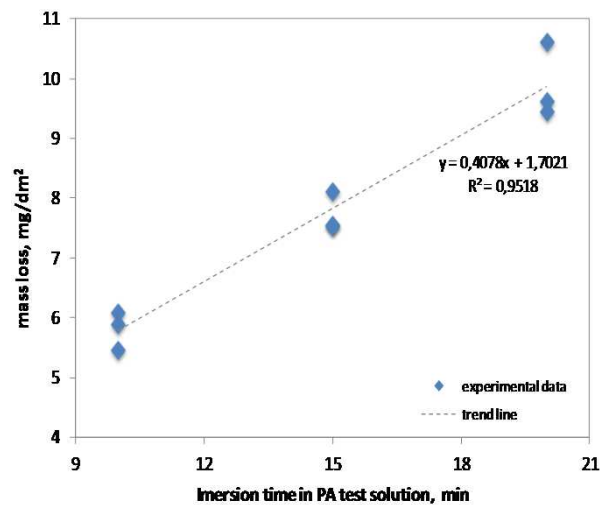
Standard test solutions and conditions for the two mass loss tests

Method	Test solution	Composition	Temperature	Immersion time
CPA (EN ISO 3210- Method 2)	Phosphoric acid / chromic acid	35 ml phosphoric acid + 20 g chromium (IV) oxide (per litre)	38°C±1°C	15 min
PA	Phosphoric acid	35 ml phosphoric acid (per litre)	38°C±1°C	15 min

PA tests conditions used to evaluate the impact on aluminium dissolution

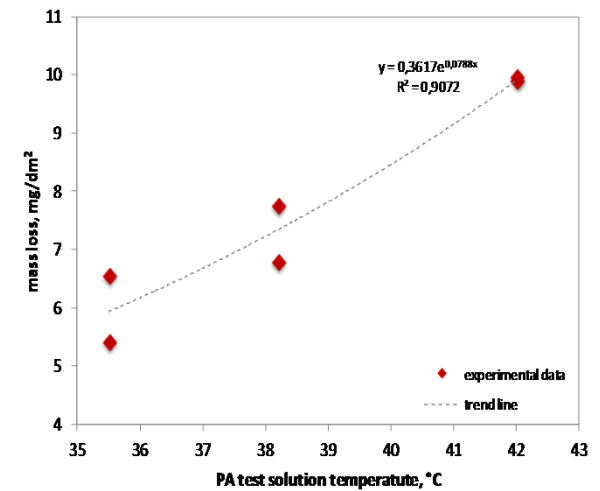
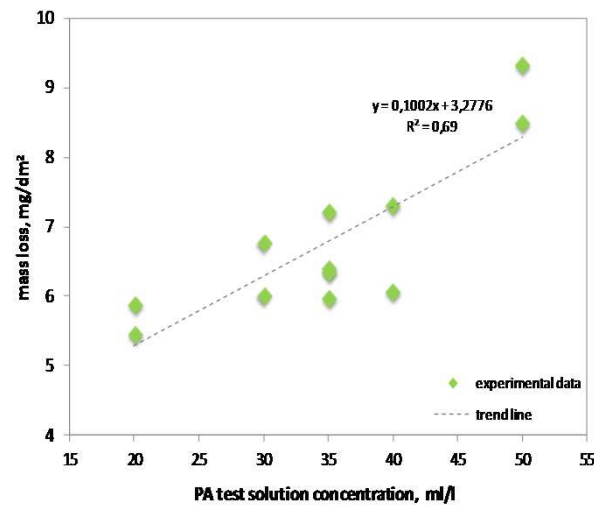
Parameter under study	Phosphoric acid test solution conditions		
	Immersion time	Temperature	Concentration
<i>Time of immersion</i>	10, 15 and 20 min	38°C±0,3°C	35 ml/l
<i>Concentration of PA test solution</i>	15 min	38°C±0,3°C	20 ml/l to 50 ml/l
<i>Temperature of PA test solution</i>	15 min	35,5°C to 42°C	35 ml/l

Study 2 Impact of PA test conditions on aluminium dissolution



Immersion time

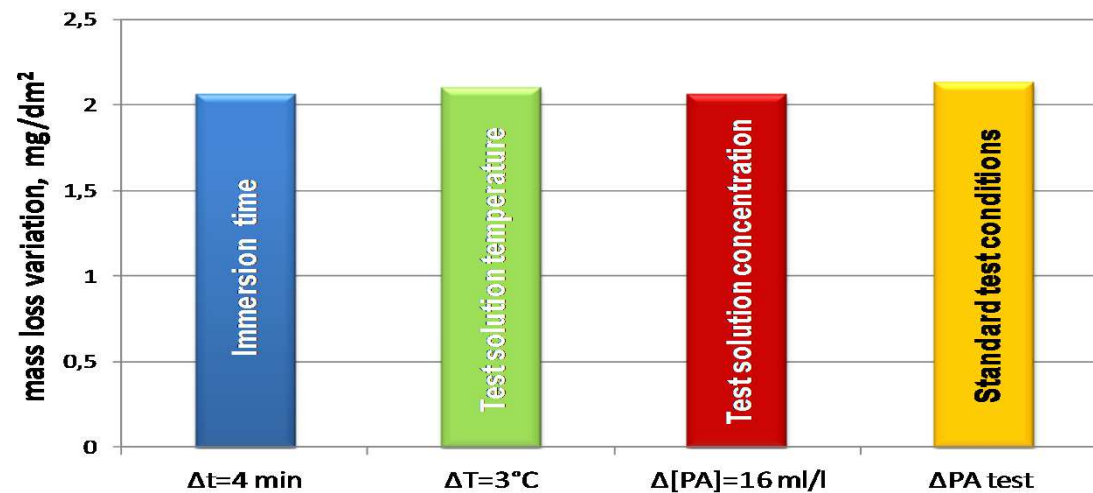
*Acid
concentration*



Temperature

Impact of PA test conditions on Al dissolution

Aluminium mass loss maximum variation rate by test condition			Average aluminium mass loss and standard deviation
Immersion time	Acid concentration of test solution	Temperature of test solution	
0,52 mg/dm ² per min	0,13 mg/dm ² per ml/l	0,70 mg/dm ² per °C	7,09±0,73 mg/dm ²



Impact of test conditions variation on aluminium mass loss variation in comparison to PA tests variation

small variations in PA test conditions have a very low impact on PA test results

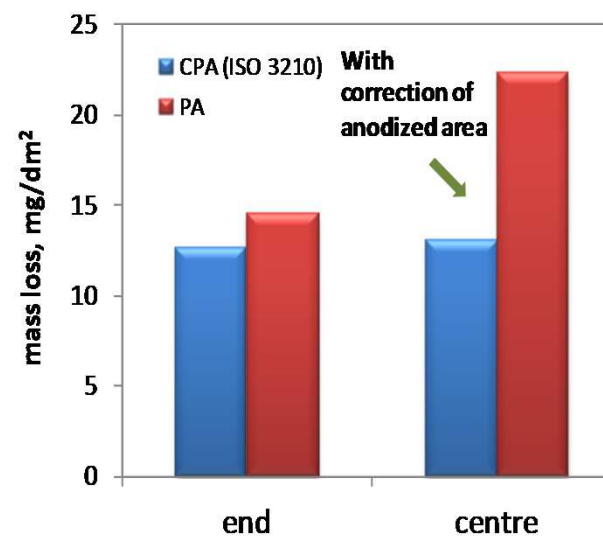
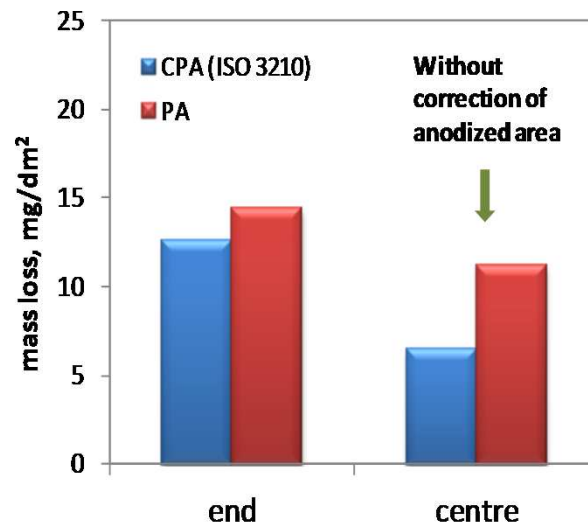
Study

Effect of bare aluminium on PA test results

PA and CPA tests carried out in partially uncoated specimens

- Cut from the end or at the middle length of a hollow profile and tested *“as produced”*
- With (2% to 45%) of bare aluminium area obtained by *chemical dissolution* or by *mechanical abrasion*

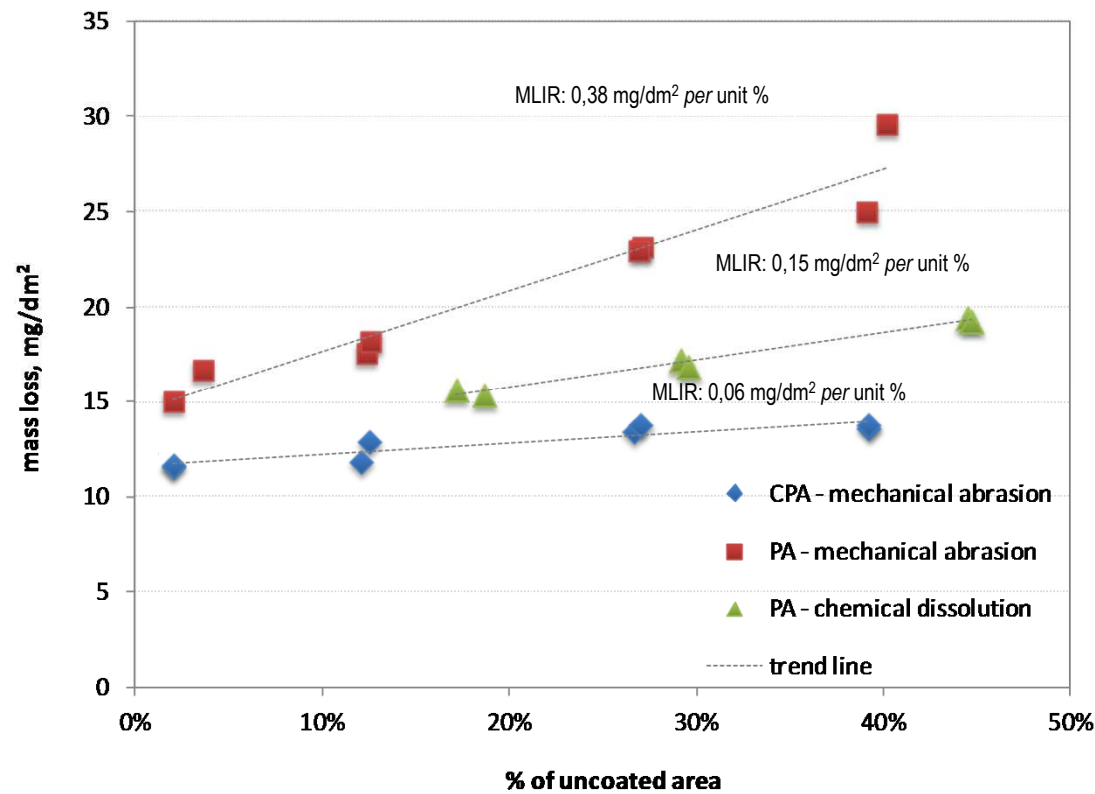
Effect of bare aluminium on PA test results



Average mass losses obtained by the CPA and PA tests for the hollow test specimens cut at different places in the profile before and after correction of the coated area

Once corrected to consider only the anodized area, a significant influence of the high % of bare aluminium area on PA test results is shown

Effect of bare aluminium and type of residual coating removing on PA test results

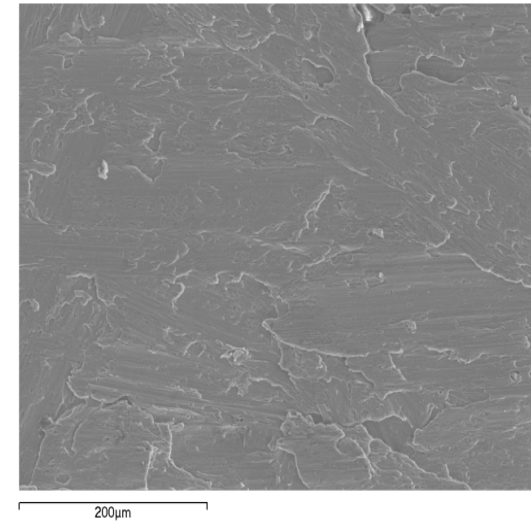


CPA and PA tests mass losses of test specimens with different % of uncoated area obtained by mechanical abrasion or by chemical dissolution
(MLIR: mass loss increasing rate calculated for each test condition)

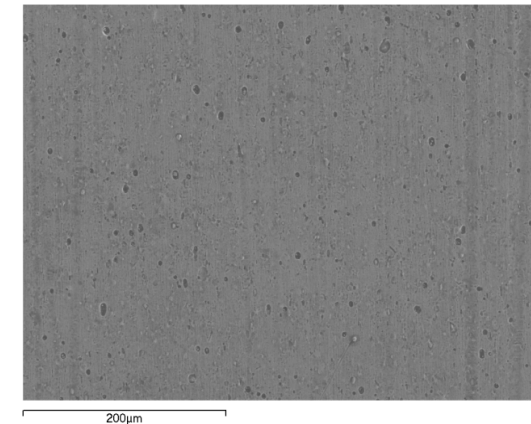
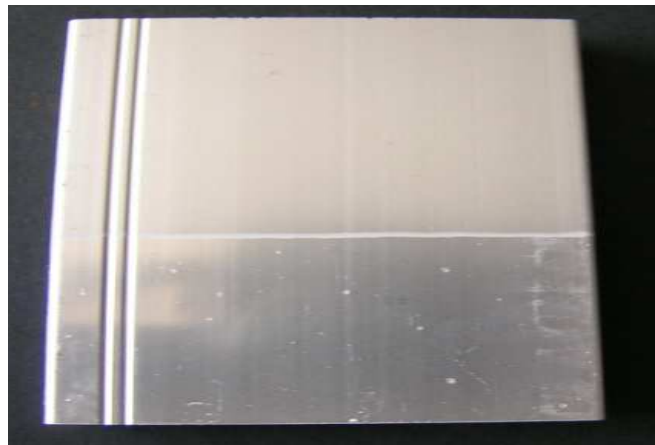
Effect of residual coating removal on PA test results



Bare aluminium
Mechanical abraded



Bare aluminium
Chemical etched



Effect of bare aluminium on PA test results



Correction

$$M_{coat} = \frac{M_{exp}(1 - Al) - 7,09 f (Al)}{(1 - Al)}$$

M_{coat} is the corrected anodic coating mass loss, in mg/dm²

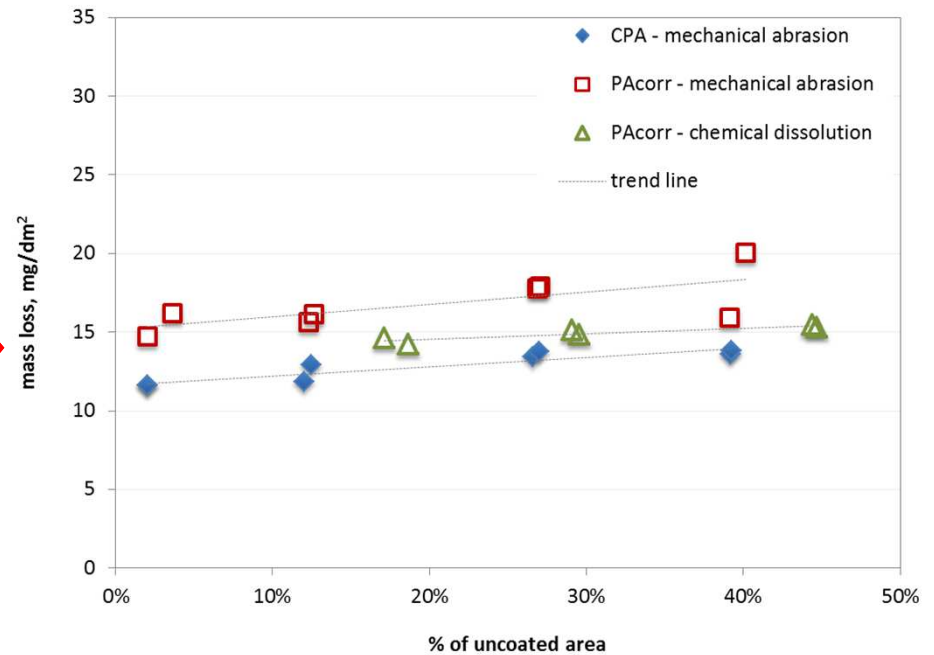
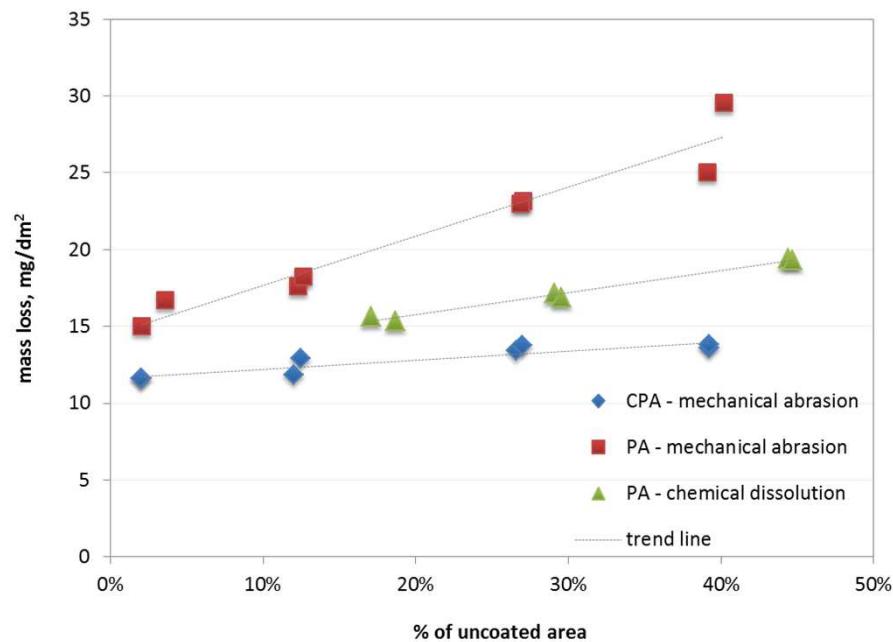
M_{exp} is the experimental mass loss, in mg/dm², calculated for the anodic coated area

Al is the proportion of uncoated surface area of the test specimen, in the range 0 to 1

7,09 is the average aluminium mass loss in PA (standard) test conditions, in mg/dm²

f is an empirical factor used to account for the aluminium surface roughness/passivation caused by the coating removal procedure used

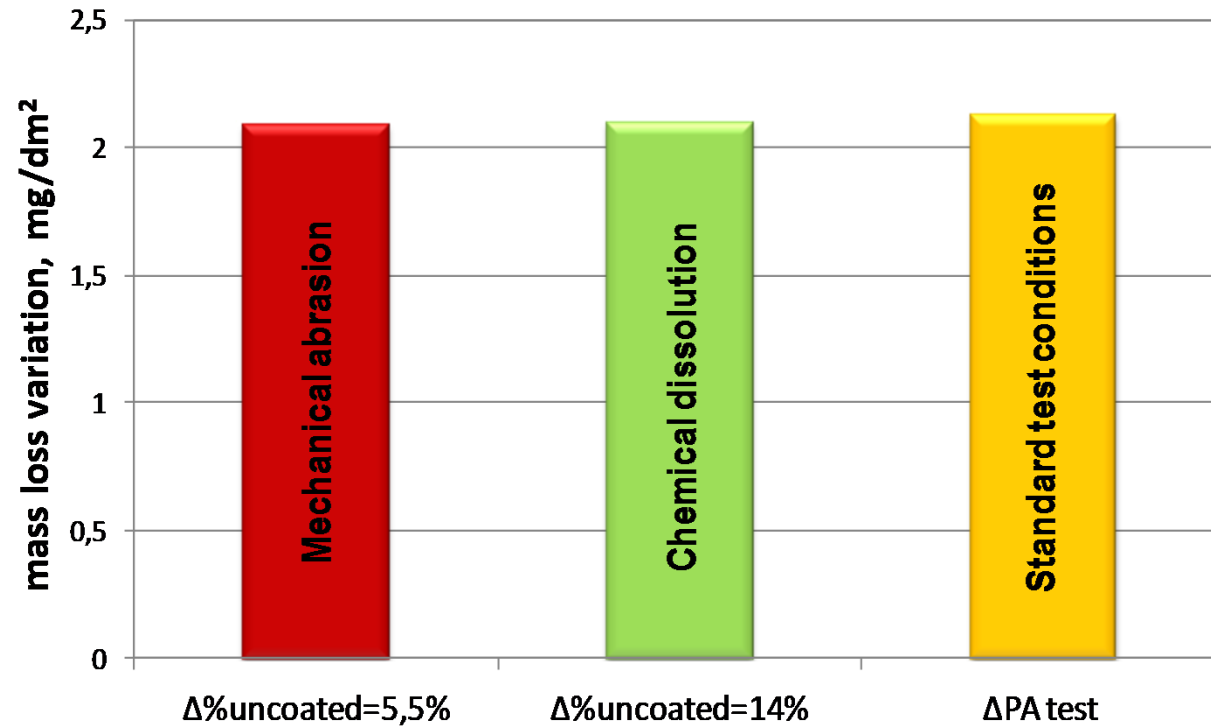
Effect of bare aluminium on PA test results



Correction of PA test mass losses by

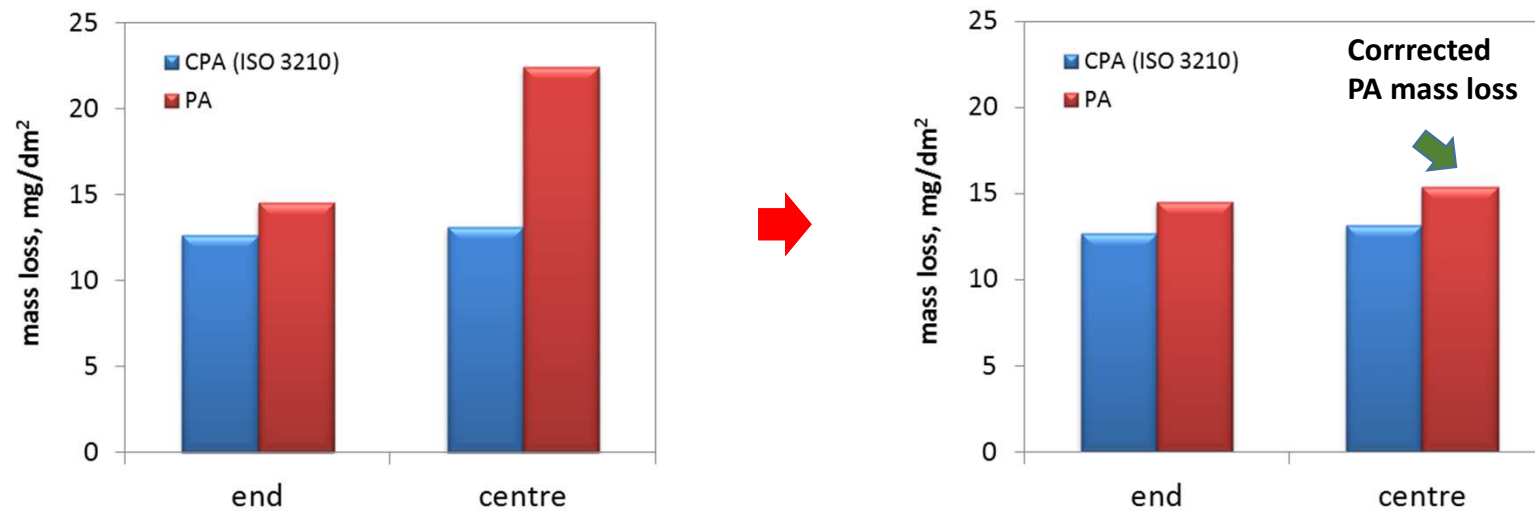
$$\frac{(\quad)(\quad)}{(\quad)}$$

Effect of bare aluminium % on PA test results



Effect of bare aluminium on PA test

Results



Correction of PA test mass losses (by eq.(1))

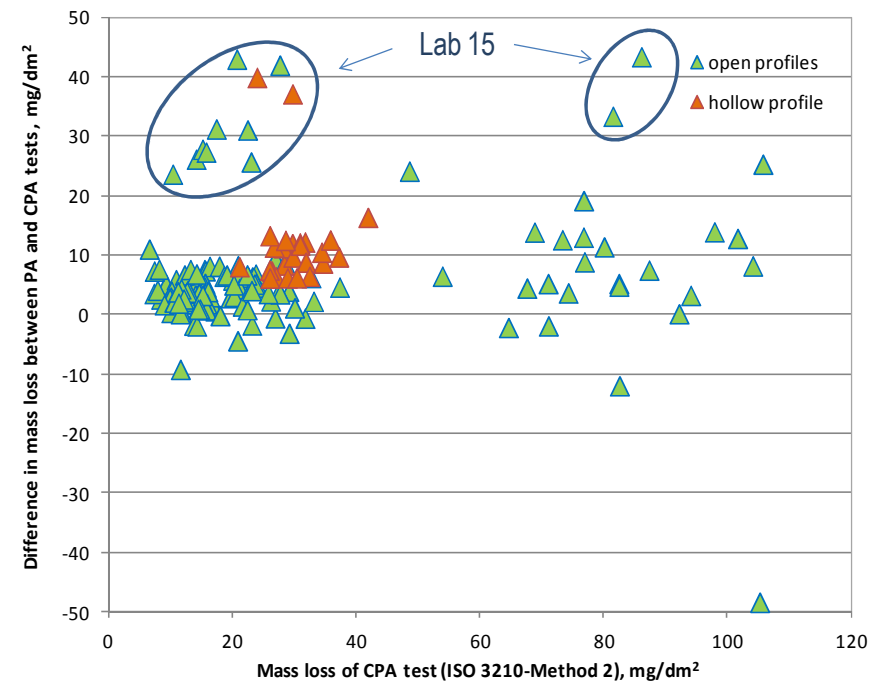
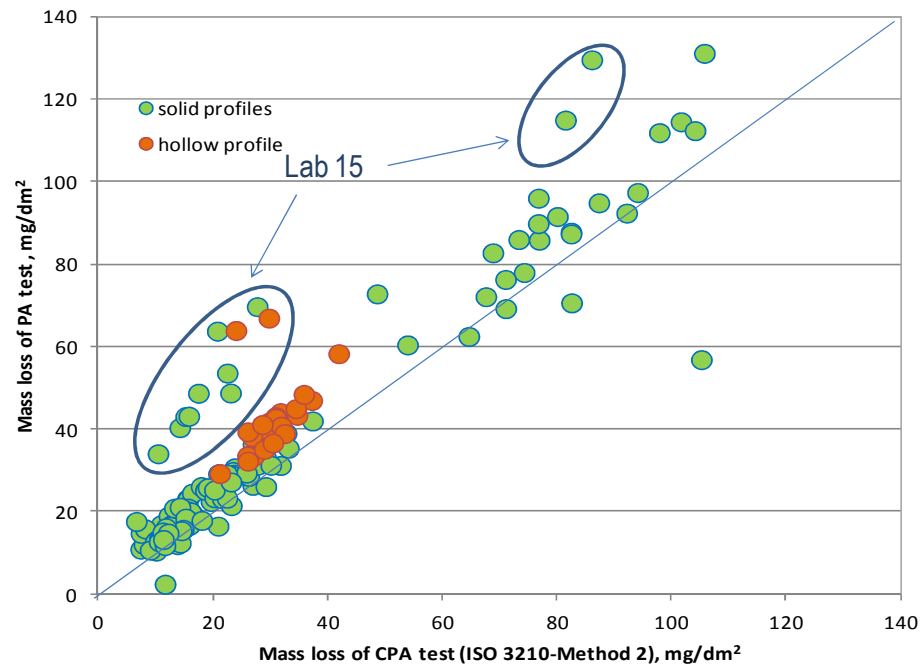
Effect of bare aluminium on PA test

Conclusions

- PA mass loss test is sensitive to the presence of bare aluminium surfaces in the test specimens.
- Small variations in PA test conditions have a very low impact on aluminium dissolution
- Aluminium contribution to mass loss values becomes significant when the uncoated area of the test specimen is above a certain limit. Process used to remove the anodic coating is relevant.
- It is possible to estimate solely anodic coating contribution to specimen mass loss using an equation. However, this estimation is highly dependent on the surface morphology and how accurate the uncoated area is quantified.

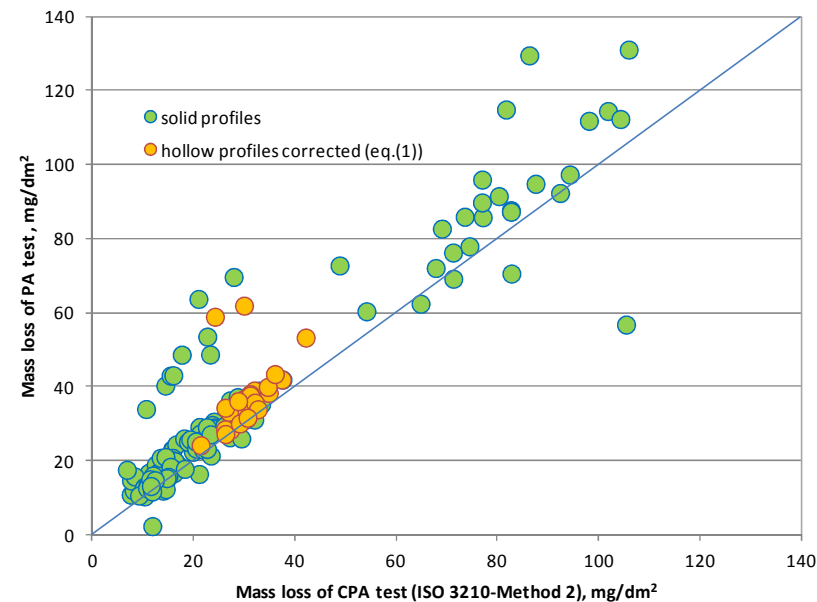
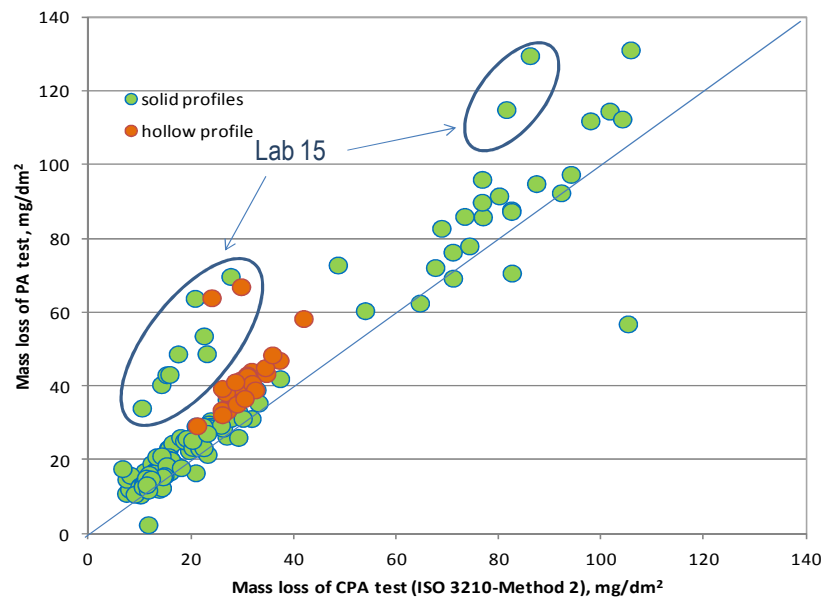
STUDY 2: 2013 RRT CPA and PA tests

Results



STUDY 2: 2013 RRT CPA and PA tests Results

RRT mass loss results from all laboratories - PA mass loss test results vs CPA mass loss test results



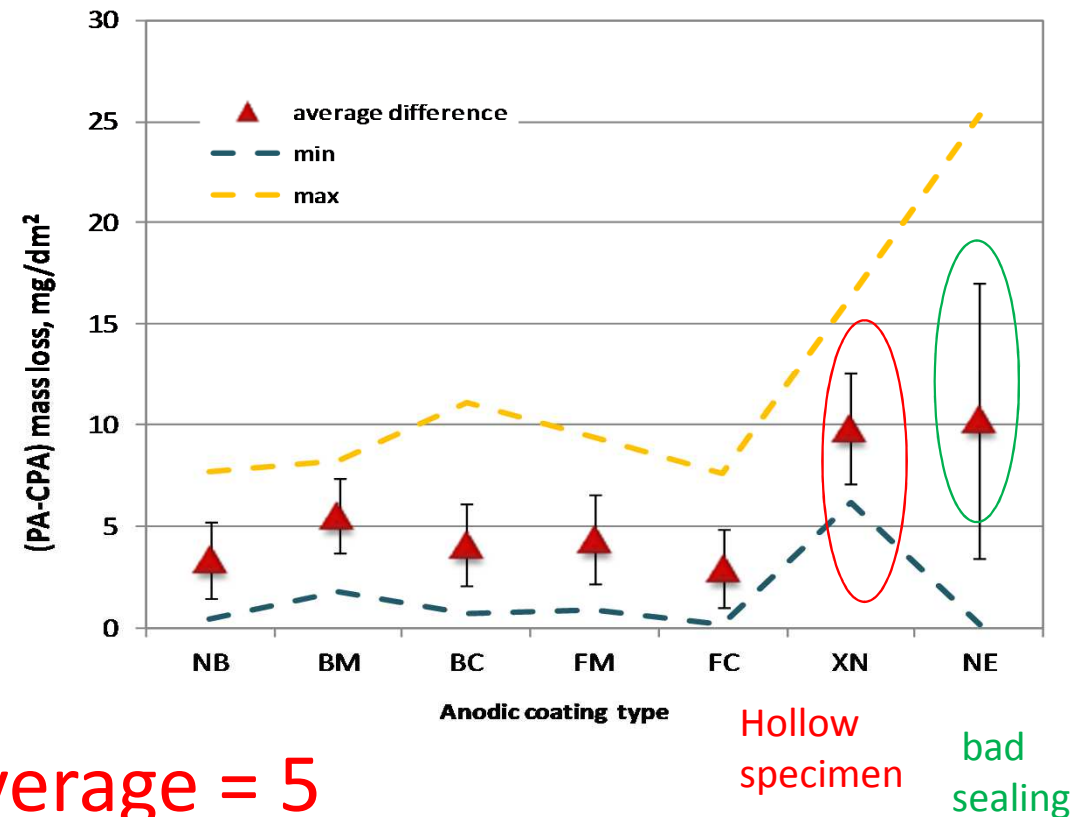
Correction of hollow profile test anodic coating PA test mass losses (by eq.(1))

PA mass loss test evidenced a similar response to CPA test

STUDY 2: 2013 RRT CPA and PA tests

Results

Anodic Coating	Profile type	Colour	Average thickness	Anodizing Temperature	Sealing	
					Process	Time/ μm
NB		Natural	19 μm	18 °C	Hot water sealing (T > 96 °C)	3 min/ μm
NE		Natural	38 μm	25 °C		2 min/ μm
BM		Bronze	18 μm	21 °C		0,6 min/ μm
BC		Bronze	18 μm	21 °C		5 min/ μm
FM		Natural	18 μm	18 °C	Cold sealing (T = 27 °C)	0,4 min/ μm
FC		Natural	14 μm	18 °C		0,8 min/ μm
XN		Natural	19 μm	17 °C	Hot water (T > 96 °C)	4 min/ μm



(PA-CPA) average = 5

STUDY 2: 2013 RRT CPA and PA tests

Results on limit criteria

Application of PA test, with the acceptance limits of 35 mg/dm² or 30 mg/dm², to assess anodic coatings sealing quality within the inter-laboratory test (excluding lab 15) in comparison to CPA test results.

PA and CPA mass loss range (values in mg/dm ²)	Number of test specimens within the range		Consequences of PA test application for the two possible mass loss limits
	solid	hollow	
PA ≤ 35 and CPA > 30	2 (30,2; 31,9) ^a	0	Acceptance of test specimens rejected by CPA test
PA ≤ 30 and CPA > 30	0	0	The same of CPA test
PA ≤ 35 and CPA = 25 to 30	7	4	Acceptance of test specimens with CPA test mass loss in the 25 to 30 mg/dm ² range
PA ≤ 30 and CPA = 25 to 30	4	0	
PA > 35 and CPA ≤ 30	2 (27,1; 28,6) ^a	7 (26,2-29,9) ^a	Increase the rejection of test specimens considered proper sealed by the CPA test
PA > 30 and CPA ≤ 30	6 (23,9-29,3) ^a	11 (26,1-29,9) ^a	

^aCPA mass loss results or results range, in mg/dm²

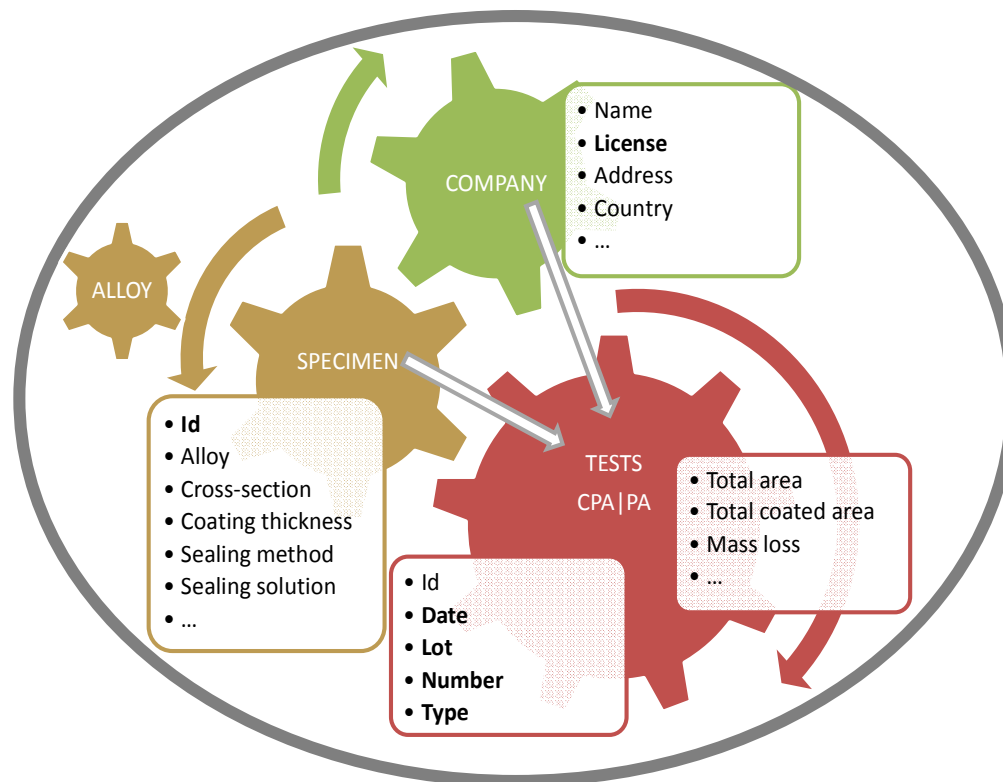
STUDY 2: 2013 RRT CPA and PA tests

Main Conclusions

- CPA and PA mass loss test methods evidence similar trends, with similar precision parameters (repeatability and reproducibility).
- For solid profiles with proper sealed anodic coatings ($\text{CPA} < 30 \text{ mg/dm}^2$):
In 95% to 100% of the tests performed, the increase in mass loss values with the PA test is inferior to 10 mg/dm^2 , and the average (PA-CPA) mass loss difference is $4,1 \text{ mg/dm}^2$ ($\pm 2,1 \text{ mg/dm}^2$). Bad sealed anodic coatings may present (PA-CPA) mass loss differences much higher than 10 mg/dm^2 and more disperse.
- The 30 mg/dm^2 acceptance limit of CPA test mass loss should be maintained for the PA test, because it assured the same level of rejections as the CPA test. It has also reduced the acceptance level of test specimens with CPA mass losses within the range of 25 to 30 mg/dm^2 .

Study 3: Analysis of CPA and PA tests results on 2013 QUALANOD Inspections

Database development



An Access® database was developed to collect data from mass loss tests of product inspections, reported by QUALANOD

Database design structure including its main tables and respective fields

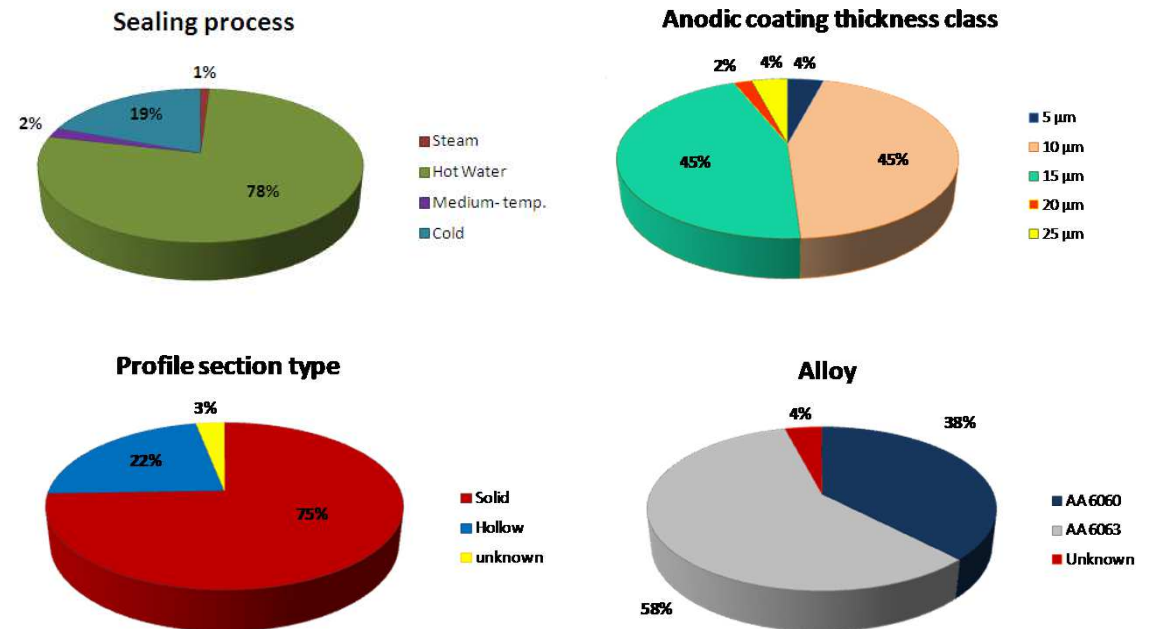
Study 3: Analysis of CPA and PA tests results on 2013 QUALANOD Inspections

Obj:PA test evaluation in real plant situation

Inspector's reporting sheet

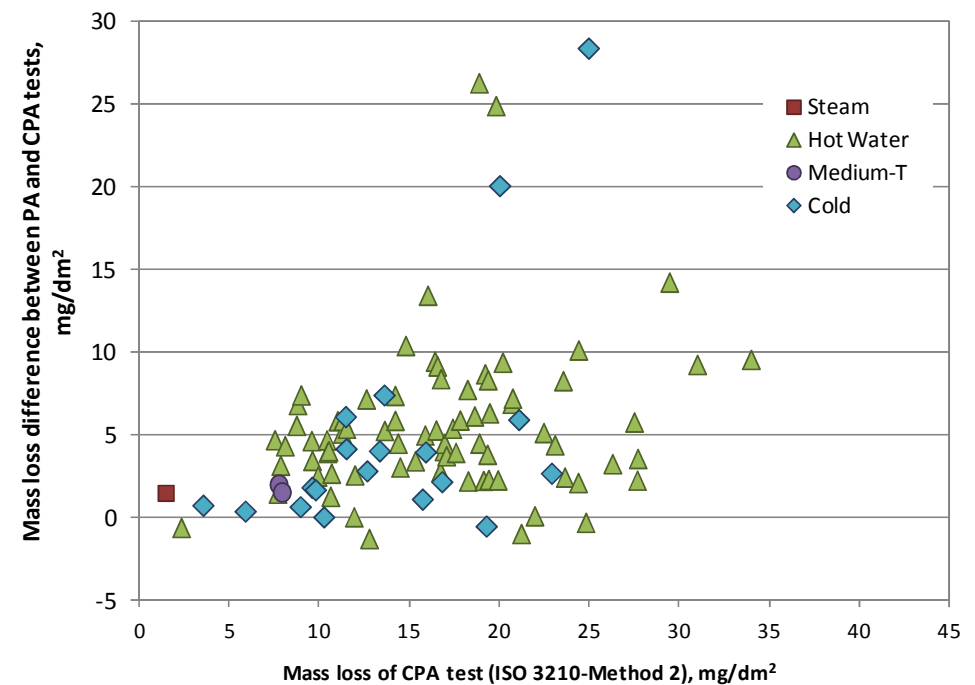
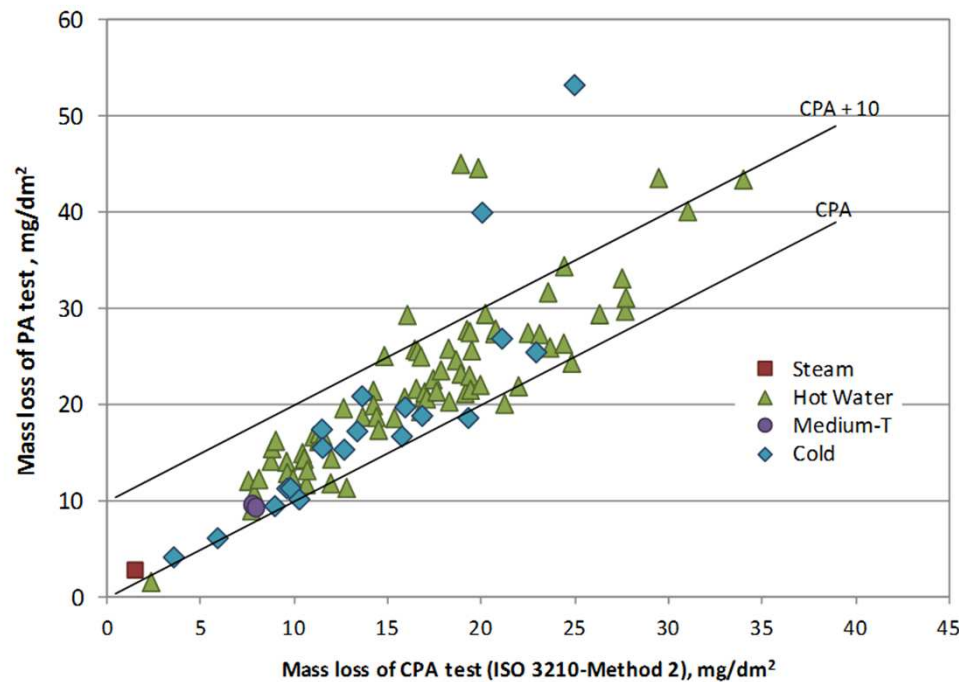
	Chromic/phosphoric acid test (ISO 3210:2010 method 2)	New phosphoric acid test
Total mass dissolved previously in the test solution (g)*		
The inspection		
Company & location		
Date of the inspection		
Alloy (eg AA6060 T6)		
Draw the cross-section of the aluminium part (this may be very approximate)		
Coating thickness class		
Sealing method (eg hot water, steam, cold sealing, medium-temperature sealing)		
Sealing solution (either Ni-based or Ni-free)		
Total area of test piece (dm ²)		
Total coated area of test piece (dm ²)		
Mass loss in the predip and test solutions (mg)		
Was the test solution stirred?		
Comments		

Test specimens characterization



Study 3: Analysis of CPA and PA tests results on 2013 QUALANOD Inspections

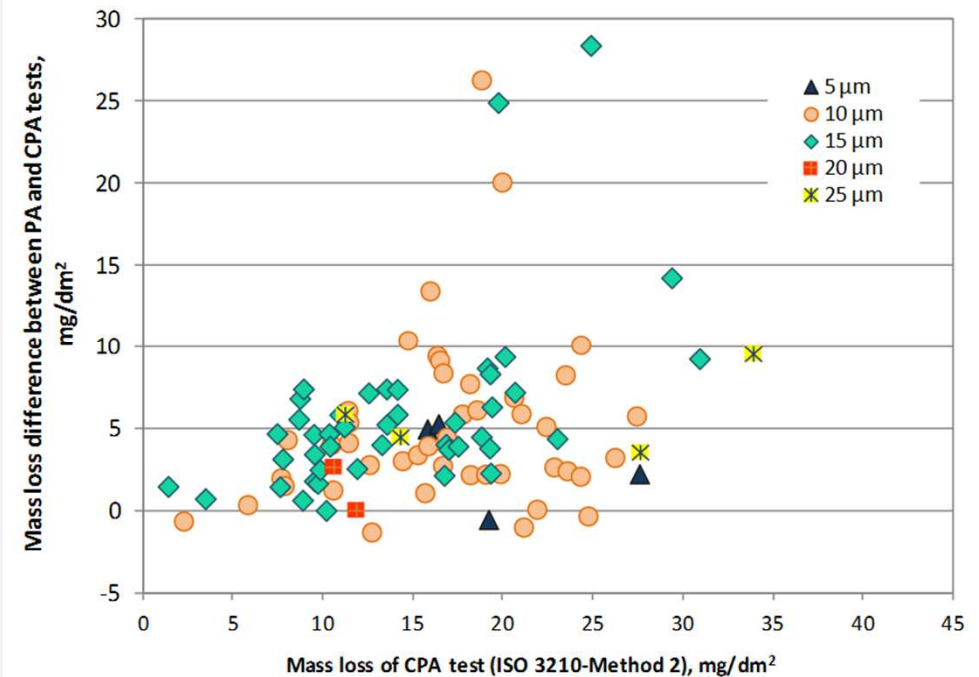
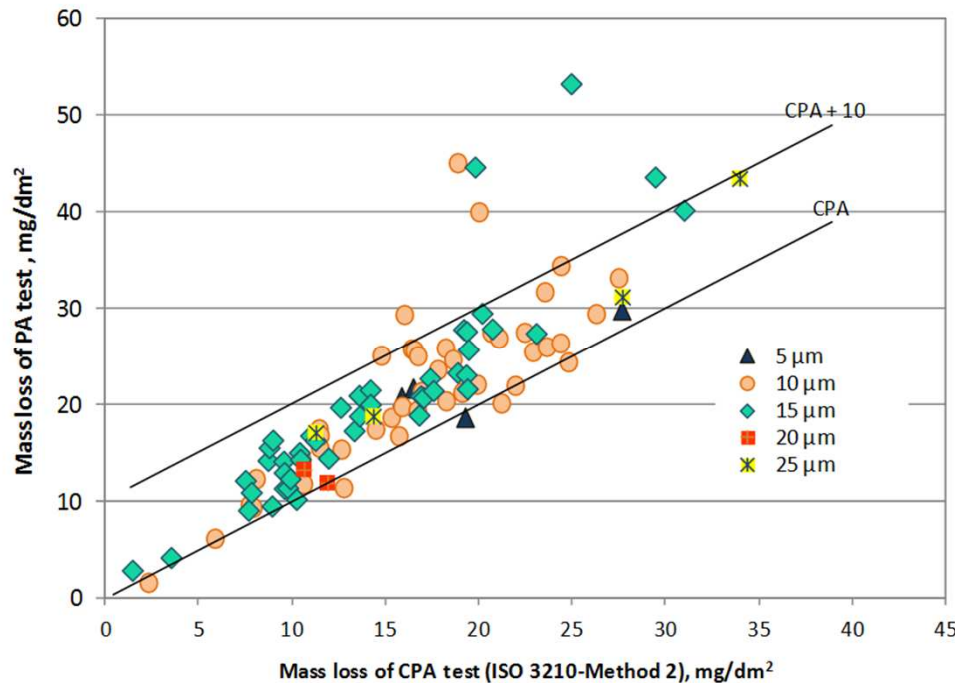
Data evaluation



PA mass loss test results vs CPA mass loss test results and correspondent mass loss differences obtained in QUALANOD inspections to anodizing plants identified by [sealing process](#)

Study 3: Analysis of CPA and PA tests results on 2013 QUALANOD Inspections

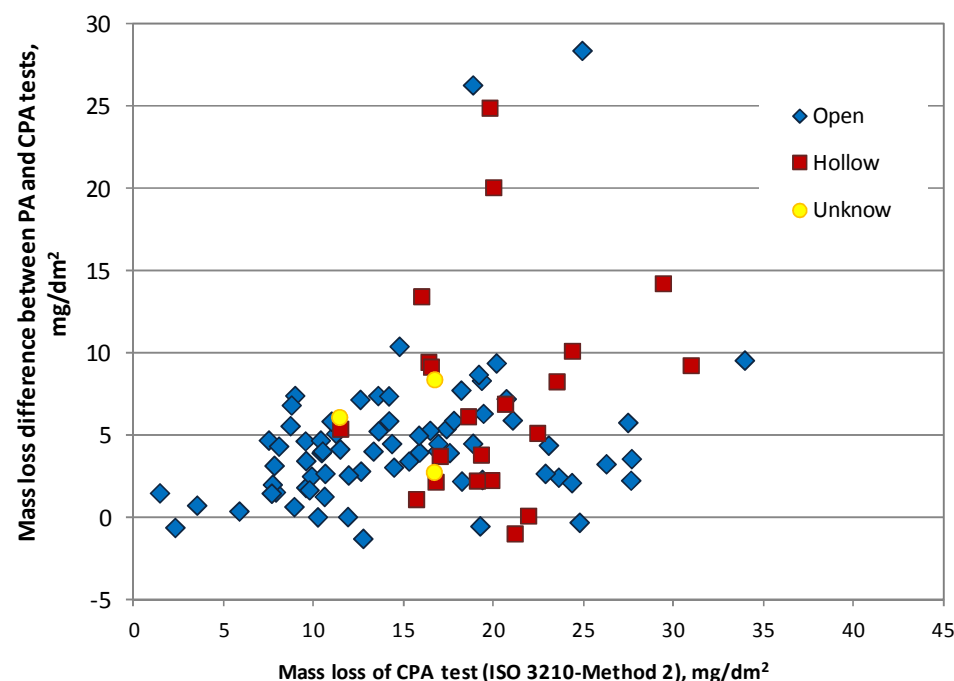
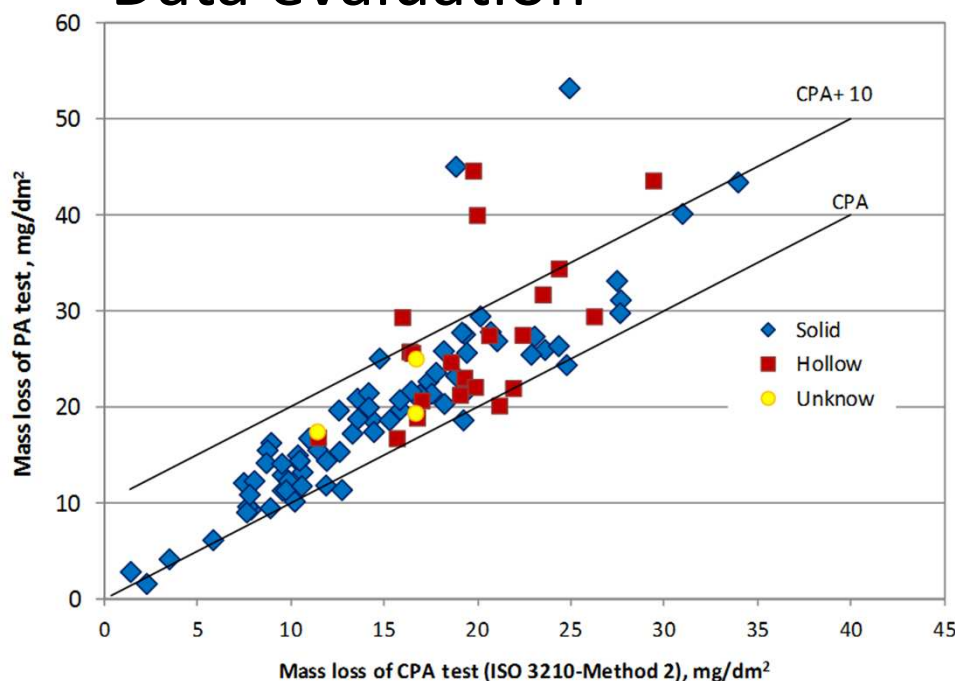
Data evaluation



PA mass loss test results vs CPA mass loss test results and correspondent mass loss differences obtained in QUALANOD inspections to anodizing plants identified by anodic coating thickness class

Study 3: Analysis of CPA and PA tests results on 2013 QUALANOD Inspections

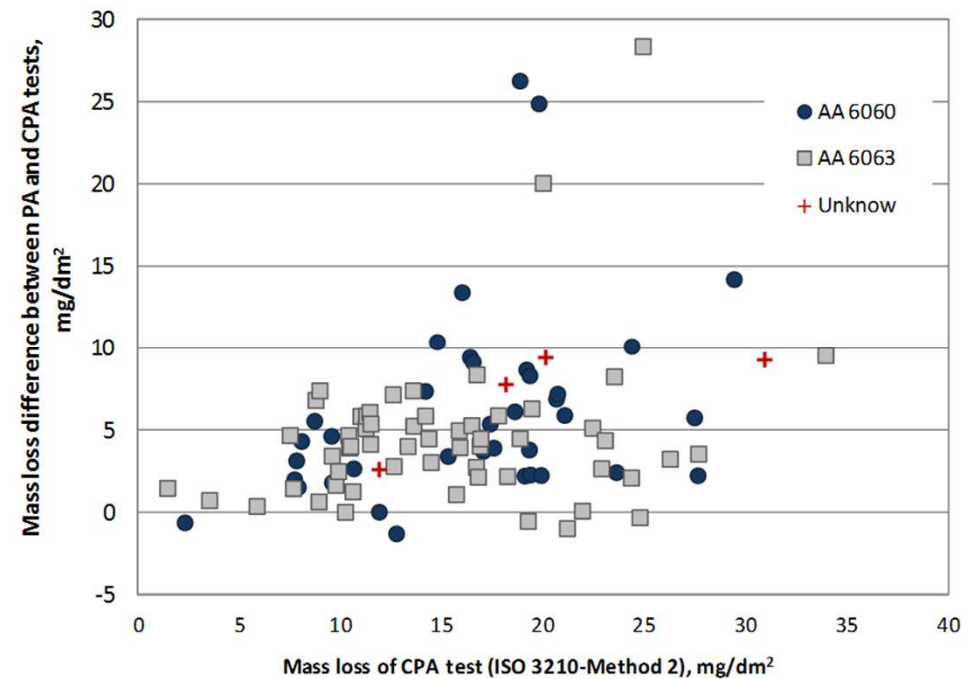
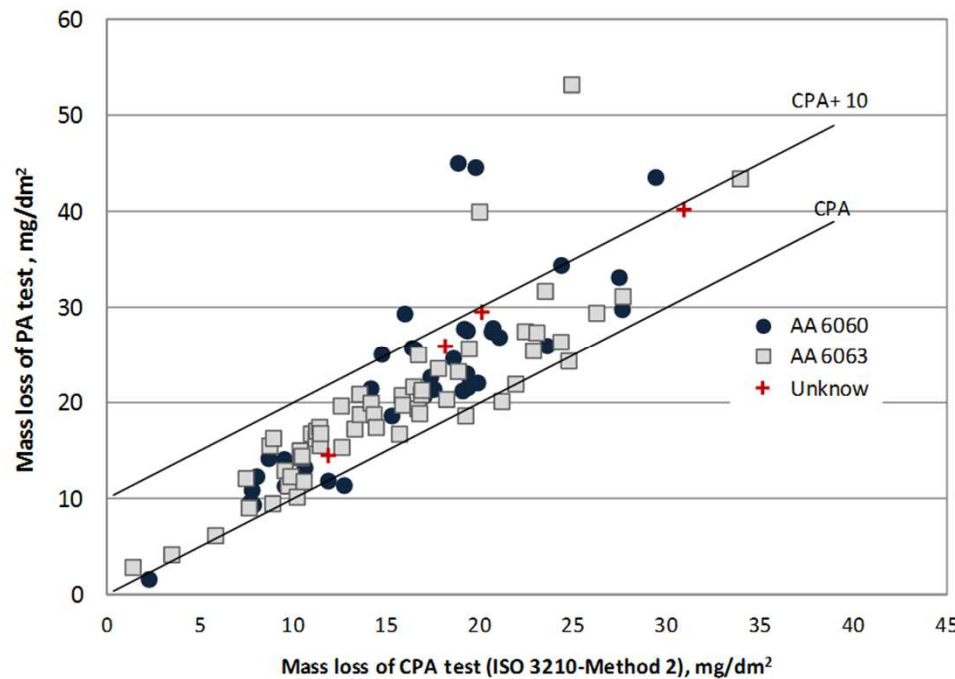
Data evaluation



– PA mass loss test results vs CPA mass loss test results and correspondent mass loss differences obtained in QUALANOD inspections to anodizing plants identified by [test specimens section type](#)

Study 3: Analysis of CPA and PA tests results on 2013 QUALANOD Inspections

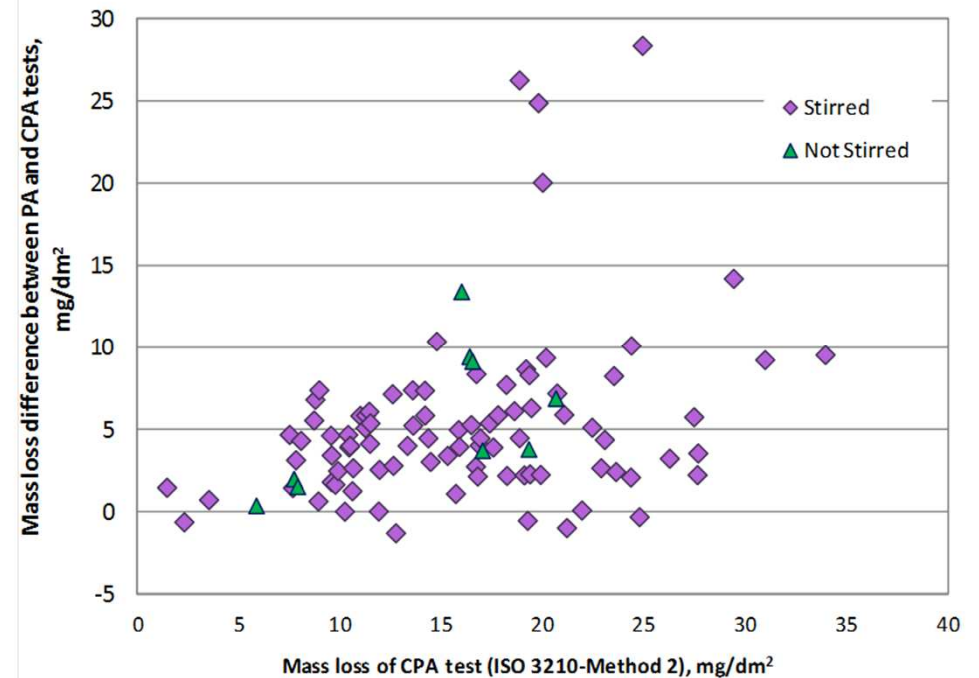
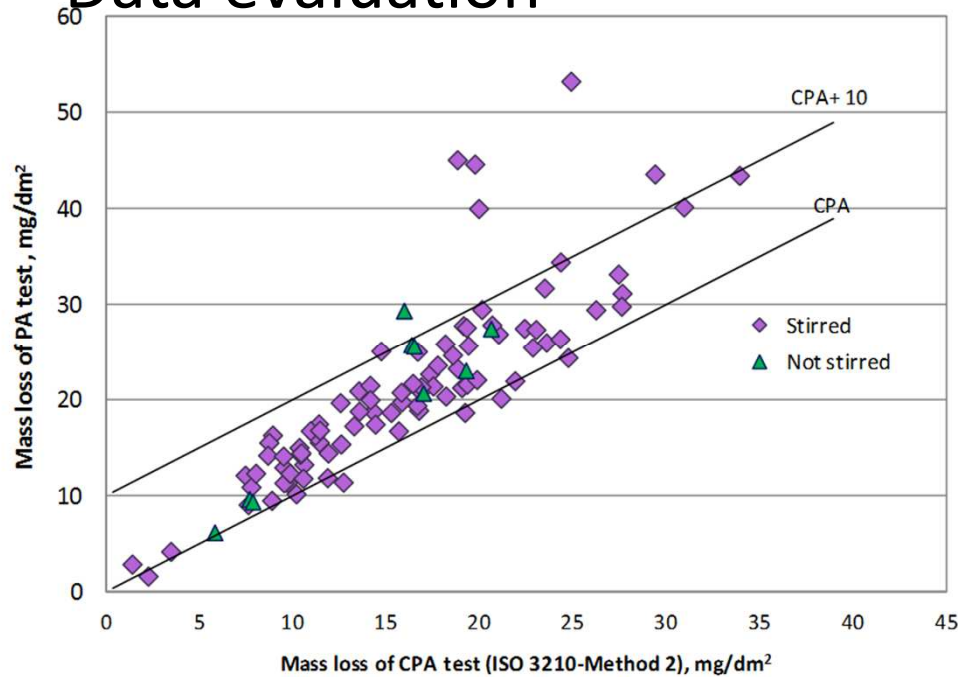
Data evaluation



PA mass loss test results vs CPA mass loss test results and correspondent mass loss differences obtained in QUALANOD inspections to anodizing plants identified by [test specimens alloy](#)

Study 3: Analysis of CPA and PA tests results on 2013 QUALANOD Inspections

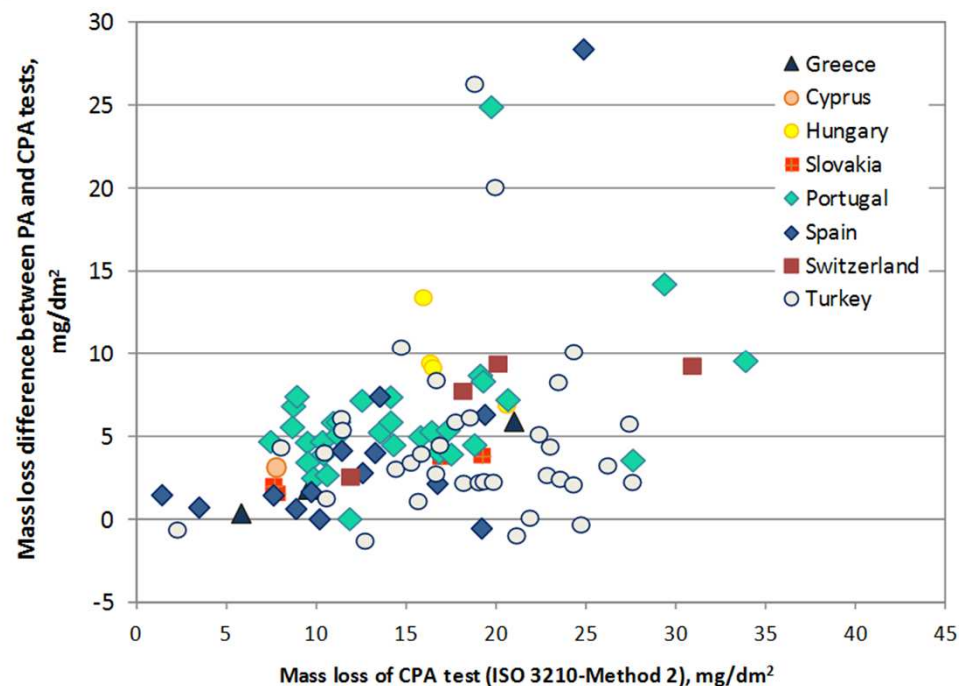
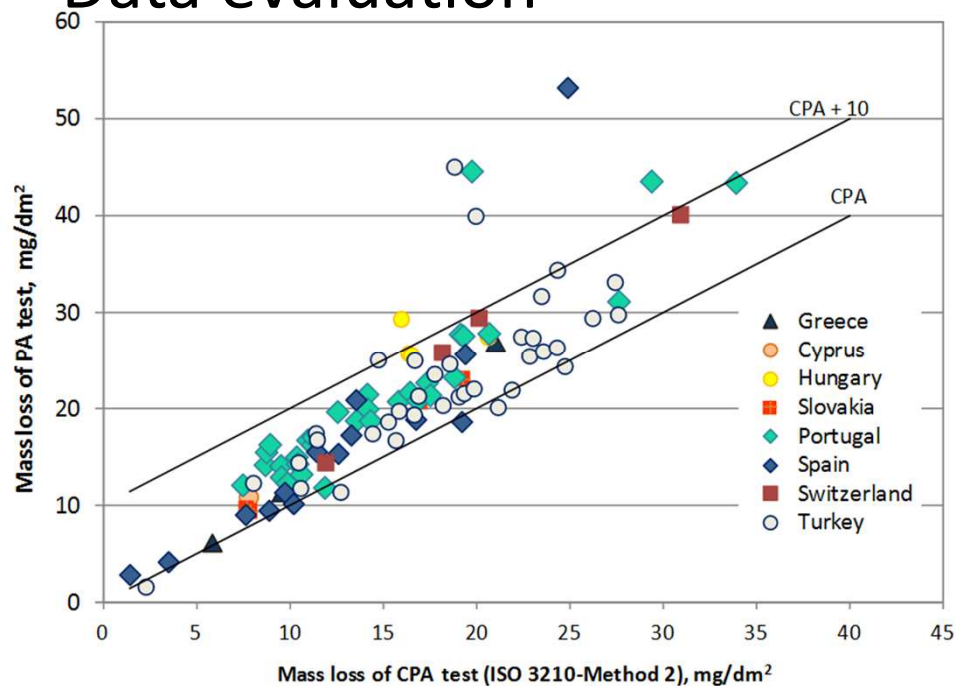
Data evaluation



PA mass loss test results vs CPA mass loss test results and correspondent mass loss differences obtained in QUALANOD inspections to anodizing plants identified by test solution stirring

Study 3: Analysis of CPA and PA tests results on 2013 QUALANOD Inspections

Data evaluation



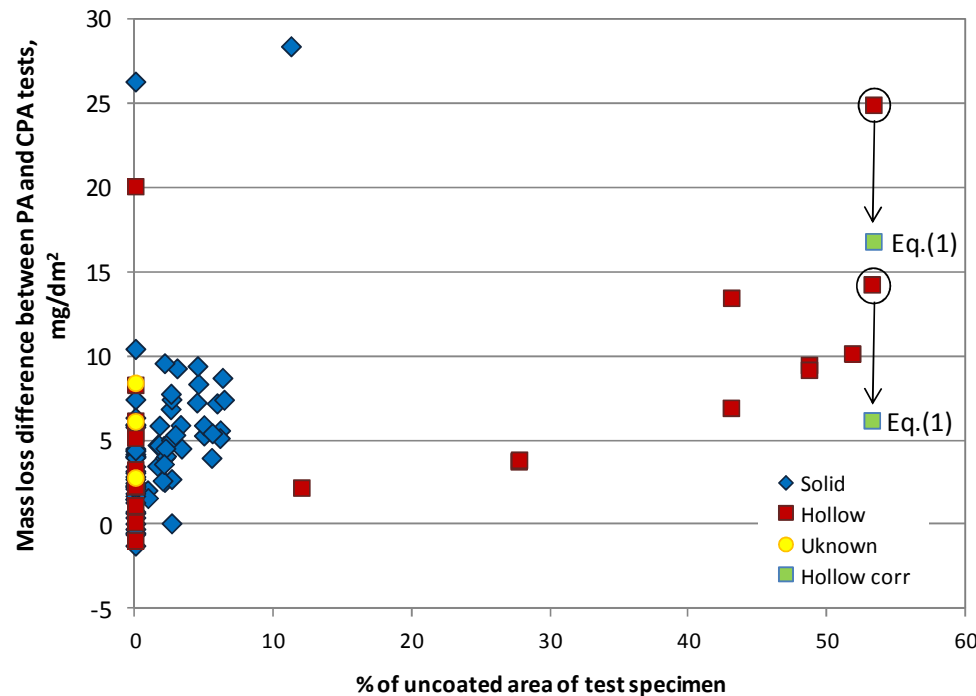
PA mass loss test results vs CPA mass loss test results and correspondent mass loss differences obtained in QUALANOD inspections to anodizing plants identified by [test specimens section provenience](#) (by country)

Study 3: Analysis of CPA and PA tests results on 2013 QUALANOD Inspections

Influence of % of uncoated area



hollow test specimens with high % of uncoated area contribute to higher dispersion and higher mass loss differences



Mass loss correction: estimation of solely anodic coating mass loss – **insufficient data available to obtain a proper estimate for all specimens**

(PA-CPA) mass loss differences vs percentage of test specimen uncoated area

(0% means that no information on total area was reported) with two hollow profiles PA test results corrected by the eq.(1) (with $f=1$)

Study 3: Analysis of CPA and PA tests results on 2013 QUALANOD Inspections

limit criteria

Application of PA test, with the acceptance limits of 35 mg/dm² or 30 mg/dm², to assess anodic coatings sealing quality within the QUALANOD inspections in comparison to CPA test results.

PA and CPA mass loss range (values in mg/dm ²)	Number of test specimens within the range		Consequences of PA test application for the two possible mass loss limits
	solid	hollow	
PA ≤ 35 and CPA > 30	0	0	The same rejection level of CPA test
PA ≤ 30 and CPA > 30	0	0	
PA ≤ 35 and CPA = 25 to 30	3	1	Acceptance of test specimens with CPA test mass loss in the 25 to 30 mg/dm ² range
PA ≤ 30 and CPA = 25 to 30	1	1	
PA > 35 and CPA ≤ 30	2 (18,8; 24,9) ^a	3 (19,7; 20; 29,4) ^a	Increase the rejection of test specimens considered proper sealed by the CPA test
PA > 30 and CPA ≤ 30	4 (18,8; 24,9; 27,4; 27,6) ^a	5 (19,7; 20; 23,5; 24,3; 29,4) ^a	

^aCPA mass loss results, in mg/dm²

Study 3: Analysis of CPA and PA tests results on 2013 QUALANOD Inspections

Main conclusions

- PA test follows CPA test response for the different types of sealing process and anodic coatings class of anodized products inspected.
- For proper sealed anodic coatings, in 94% of the tests performed, the increase in mass loss values obtained with the PA test in relation to CPA test is inferior or equal to 10 mg/dm^2 , and in average is $5,3 \text{ mg/dm}^2 (\pm 5,1 \text{ mg/dm}^2)$.
- No specific cause was attributed for the variation of (PA-CPA) mass loss differences within the 10 mg/dm^2 range. However, higher mass loss differences can be associated with hollow test specimens.
- The 30 mg/dm^2 acceptance limit of CPA test mass loss should also be maintained for the PA test. This criterion assures the same level of rejection of CPA tests and reduces the acceptance level of test specimens with high CPA mass losses, mainly within the range of $25 - 30 \text{ mg/dm}^2$.

PA test is candidate for CPA test replacement

Conclusions from studies done

- Phosphoric acid (PA) immersion test confirmed as a very promising Cr-free alternative mass loss test to replace the phosphoric acid/chromic acid (CPA) immersion test.
- The same maximum mass loss limit of the CPA test (30 mg/dm²) should be adopted for the PA test to assure the same sealing quality level requirement.
- Some limitations exist for the application of the PA test to hollow profiles for sealing evaluation, especially to those with significant percentage of uncoated area over 10 - 20%. In these cases, it requires:
 - *mass loss correction (ex.: using eq. or similar);*
 - *if a rigorous correction is not possible then the uncoated surfaces should be masked before test.*

Future developments

PA test as candidate for CPA test replacement

To address the question of bare aluminium limitation

- Study of a corrosion inhibitor more environmental compliant than Cr(VI) to the PA test solution, but equally able to prevent aluminium dissolution
- Masking materials evaluation

To address the question of (PA-CPA) mass losses differences variability

- Within QUALANOD inspections collect information about production variables that may influence anodic coatings properties (porosity, hardness, etc.) like: anodizing temperature and current density, and also about coating properties such as its actual thickness and hardness (in above 20 μm).

Proposal to improve the Reporting sheet

	Chromic/phosphoric acid test (ISO 3210:2010 method 2)	New phosphoric acid test
Total mass dissolved previously in the test solution (g)*	- calculations of mass loss (e.g. $X \div Y = Z \text{ mg/dm}^2$) it can be used to check if the results are corrects; - or remove this line.	
The inspection		
Company & license	- Company and licence number.	
Date of the inspection		
Alloy (eg AA6060 T6)		
The cross-section of the aluminium part open or close? (draw very approximate)	- writing always if it's open or close cross-section; - draw or adding cross-section layout	
Coating thickness class, measured thickness , abrasion test and colour	- writing in addition the coating colour - thickness measured in same profile - Abrasion (BS) test result in same profile	
Sealing method (eg hot water, steam, cold sealing, medium-temperature sealing)		
Sealing solution (either Ni-based or Ni-free)		
Total area of test piece (dm ²)		
Total coated area of test piece (dm ²)		
Mass loss in the predip and test solutions (mg)		
Was the test solution stirred?		
Comments: - clarification about presented results - preparation of test surface in case of close cross-section (how the test surface was prepared if the interior surface was removed and how)		

* ISO 3210:2010 states that the test solution should not be used after more than 4,5 g of anodic coating have been dissolved per liter of solution; of course, the chromic/phosphoric acid solution does not dissolve aluminium metal. We do not know how this criterion could be applied to the new phosphoric acid test where both anodic coating and aluminium metal might be dissolved. As an approximation, the total mass dissolved is the sum of the mass losses from previous tests carried out with the solution.