



LABORATÓRIO NACIONAL
DE ENGENHARIA CIVIL

(STUDY ON ANODIC OXIDE COATING SEALING QUALITY
ASSESSMENT METHODS FOR PHOSPHORIC/CHROMIC ACID
IMMERSION TEST REPLACEMENT

Proposal for a new test specification)

**ESTUDO DE MÉTODOS DE ENSAIO PARA AVALIAR
A QUALIDADE DA COLMATAGEM DE
REVESTIMENTOS DE OXIDAÇÃO ANÓDICA PARA
SUBSTITUIÇÃO DO ENSAIO DE IMERSÃO COM
SOLUÇÃO FOSFOCRÓMICA**

Proposta de um novo método de ensaio

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Testing methods

- **CPA test** (*reference method*) – Assessment of quality of sealed anodic oxidation coatings by measurement of the mass loss after immersion in phosphoric acid/chromic acid solution for 15 min, with prior acid treatment (EN ISO 3210:2010-Method 2).

- **PA test** – Assessment of quality of sealed anodic oxidation coatings by measurement of the mass loss after immersion in phosphoric acid solution for 15 min. This test solution corresponds to the EN ISO 3210:2010 – Method 2 acid test solution without the addition of chromium (VI) oxide (no standard).

- **SA test** – Assessment of quality of sealed anodic oxidation coatings by measurement of the mass loss after immersion in sulphuric acid solution at 38 °C and 50 °C for 15 min.

- **AASA test** – Assessment of quality of sealed anodic oxidation coatings by measurement of the loss of mass after immersion in a mixture of acetic glacial acid and sodium acetate solution at boiling point for 15 minutes. Usually [6], for this type of acid solution, a maximum mass loss of 20 mg.dm⁻² is permitted to consider the anodic coating proper sealed

General characteristics of the test specimens

Coating type	Anodization	Sealing process	Additive	Sealing time
MT07	T < 19 °C	Midtemp sealing	Alfiseal 969	15 min
MT4	T < 19 °C	Midtemp sealing	Alfiseal 969	75 min
HS07	T < 19 °C	Hot sealing	P3 Almeco Seal	15 min
HS1	T < 19 °C	Hot sealing	P3 Almeco Seal	15 min
HS3	T < 19 °C	Hot sealing	P3 Almeco Seal	60 min
HS4	T = 25 °C	Hot sealing	P3 Almeco Seal	75 min
HS5	T < 19 °C	Hot sealing	P3 Almeco Seal	75 min
HS2	T < 19 °C	Hot sealing	PR (ALSAN)	40 min
HS3A	T < 19 °C	Hot sealing	PR (ALSAN)	60 min

Specimens anodized by: Navarra, Metalfer and Alfasul

Test solutions and conditions of the different immersion tests of the comparative study

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	15 min
				(I) 20 min ^(a)
PA ^(b)	Phosphoric acid	35 ml phosphoric acid (per litre)	38 °C	15 min
				(I) 20 min ^(a)
SA-38°C ^(b)	Sulphuric acid	15 % sulphuric acid	38 °C	15 min
SA-50°C ^(b)	Sulphuric acid	15 % sulphuric acid	50 °C	15 min
AASA ^(b)	Acetic glacial acid and sodium acetate	100 ml acetic glacial acid + 0,5 g sodium acetate (per litre)	Boiling point	15 min

(a) Additional test conditions involving the increase of immersion time in relation to EN ISO 3210-Method 2 experimental procedure

(b) Tests carried following the EN ISO 3210-Method 2 experimental procedure changing only the test solution

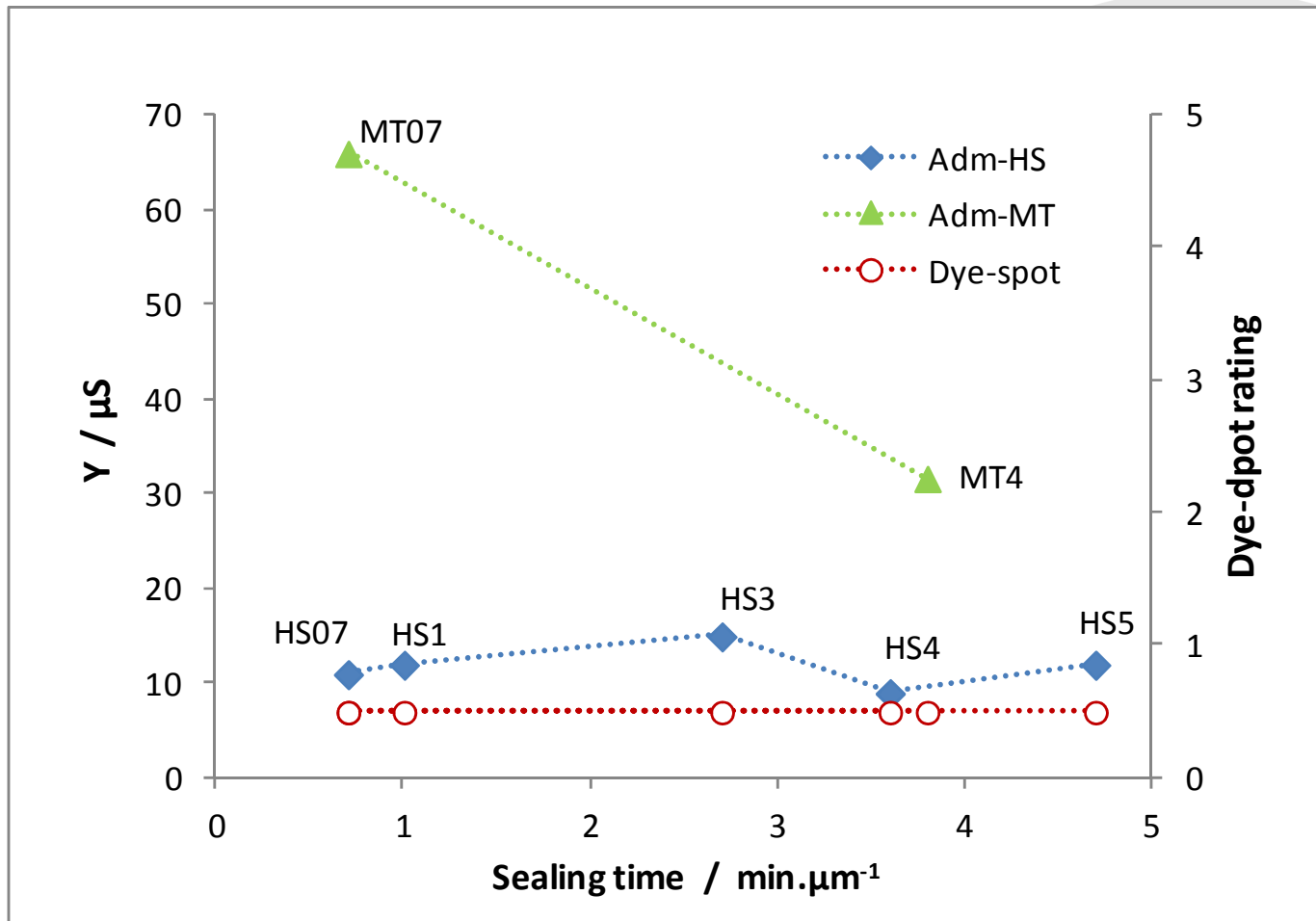
Experimental program resumed by immersion test method and coating type

Coating type	test method						
	CPA	PA	SA-38°C	SA-50°C	AASA	CPA-I	PA-I
MT07	+	+	+	+	+	-	-
MT4	+	+	-	+	+	-	-
HS07	+	+	-	+	+	+	+
HS1	+	+	+	+	+	-	-
HS2	+	+	-	-	-	-	-
HS3	+	+	+	+	+	-	-
HS3A	+	+	-	-	-	+	+
HS4	+	+	+	+	+	-	-
HS5	+	+	-	+	+	-	-

Test specimen's anodic coating characteristics (average values)

Coating type	Thickness (EN ISO 2360)	Sealing time ^(a) (min/ μm)	Sealing quality assessment	
			Admittance test – Y (EN ISO 2931)	Dye-spot test class (EN ISO 2143)
MT07	22 μm	0,7	66 μS	0-1
MT4	20 μm	3,8	32 μS	0-1
HS07	21 μm	0,7	11 μS	0-1
HS1	15 μm	1,0	9 μS	0-1
HS2	23 μm	2,0	-	-
HS3	22 μm	2,7	12 μS	0-1
HS3A	23 μm	2,6	-	-
HS4	21 μm	3,6	15 μS	0-1
HS5	16 μm	4,7	12 μS	0-1

Admittance and Dye-spot tests results for different sealing times

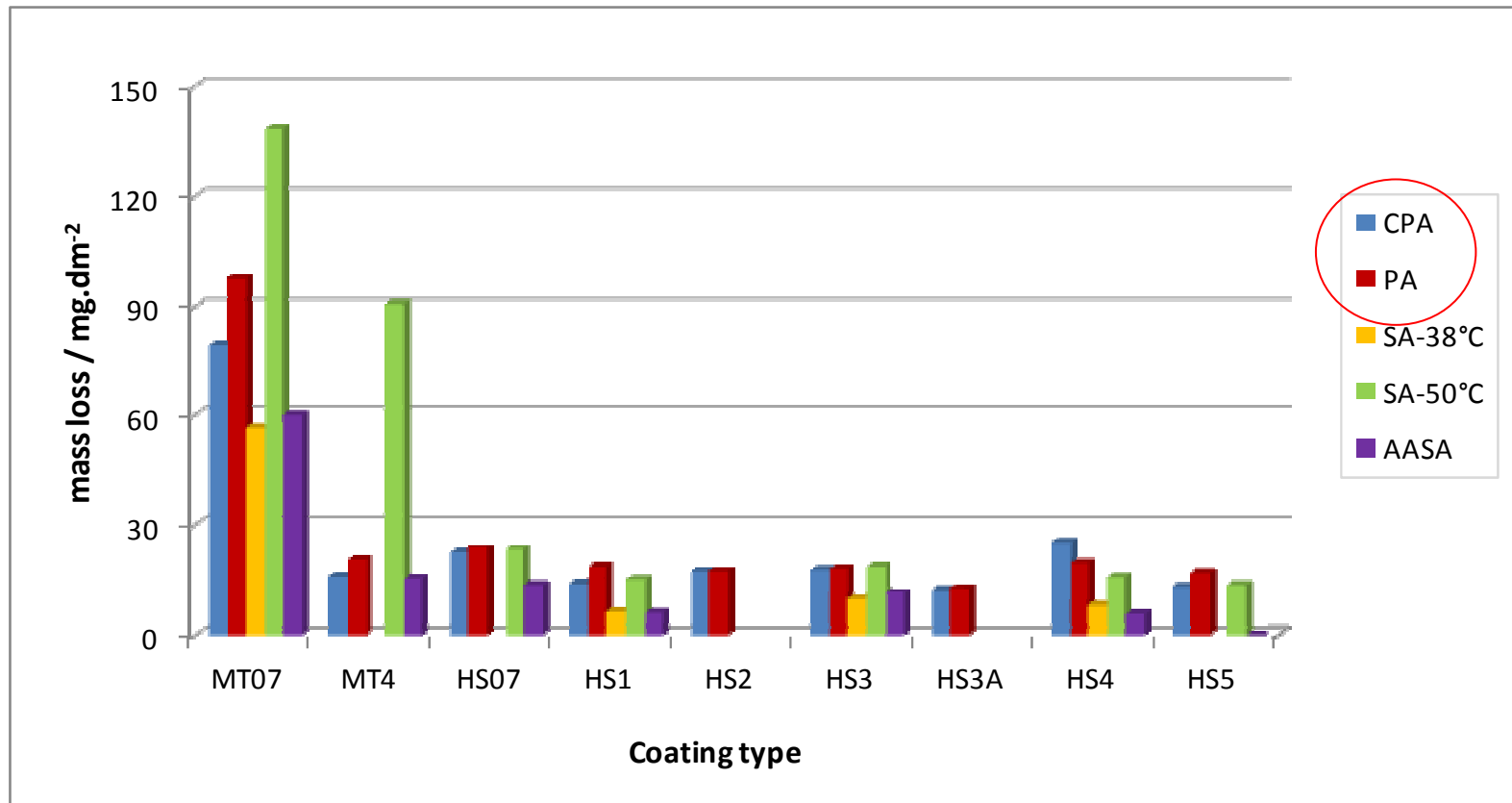


Average weight loss results and respective standard deviation obtained by the different immersion tests for aluminium and anodized test specimens

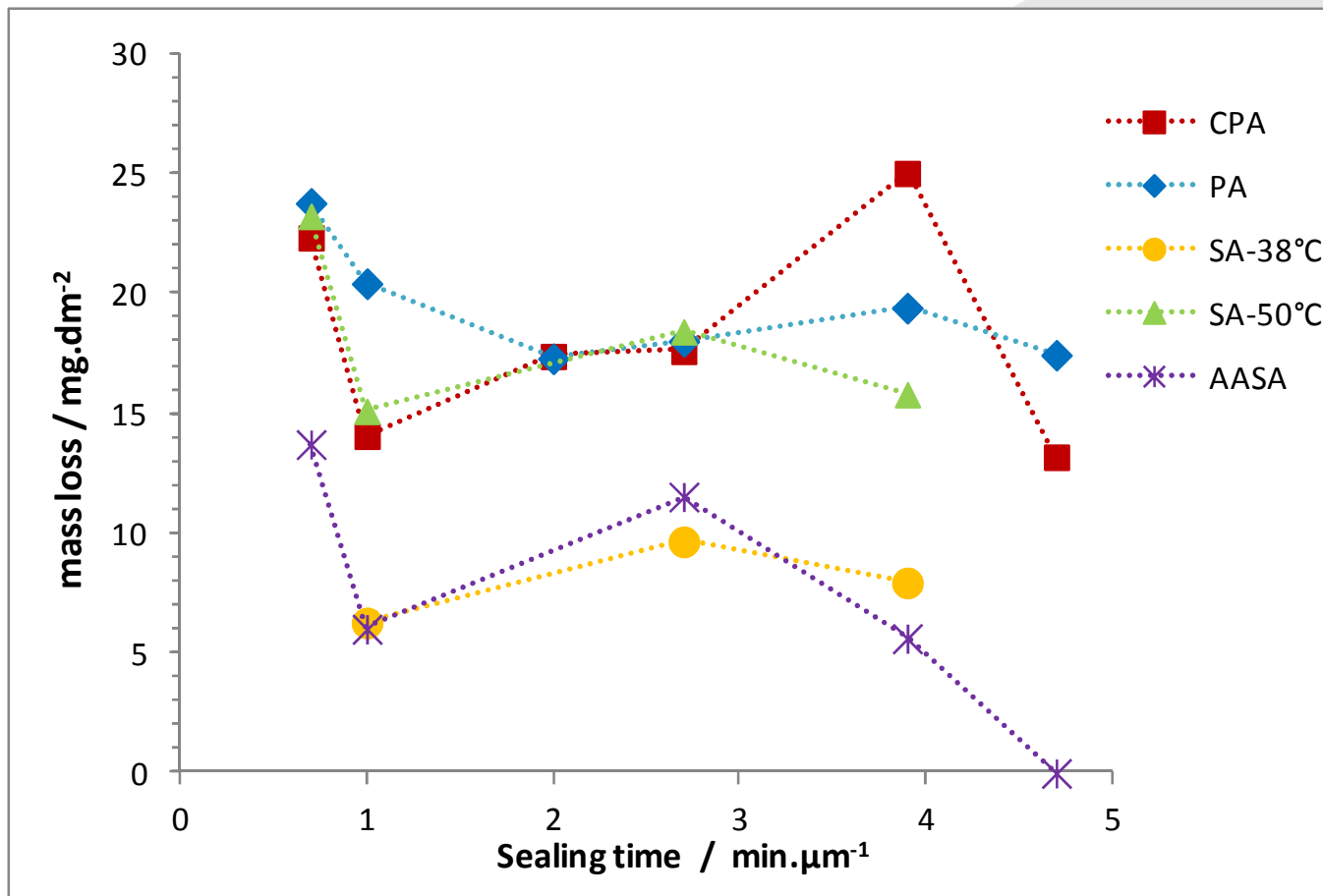
Coating type	Average weight loss by test method / mg.dm ⁻²				
	CPA	PA	S.A. 38 °C	S.A. 50 °C	A.A.S.A.
Ø - aluminium	0,4±0,2	5,3±0,2	2,6±0,1	6,0±0,3	6,1±0,8
MT07	79±11	97±9	57±3	138±5	60±7
MT4	15,9±0,6	20,4±0,8	-	91±2	15,4±1,4
HS07	22,3±0,3	23,7±1,5	-	23,2±0,6	13,7±0,8
HS1	14,0±0,4	18,5±0,4	6,3±0,1	15,1±0,7	6,0±0,8
HS2	17,4±0,3	17,3±1,1	-	-	-
HS3	17,6±0,3	18,0±0,9	9,7±1,1	18,4±1,1	11,5±0,5
HS3A	12,3±0,6	12,8±1,0	-	-	-
HS4	25.30*	19,4±0,9	8,0±0,4	15,8±1,8	5,6±0,9
HS5	13,19±0,02	16,9±0,3	-	13,6±1,4	(2,7±0,3)×10 ⁻³

* 1 test specimen

Mass losses obtained by the different immersion tests for each coating type

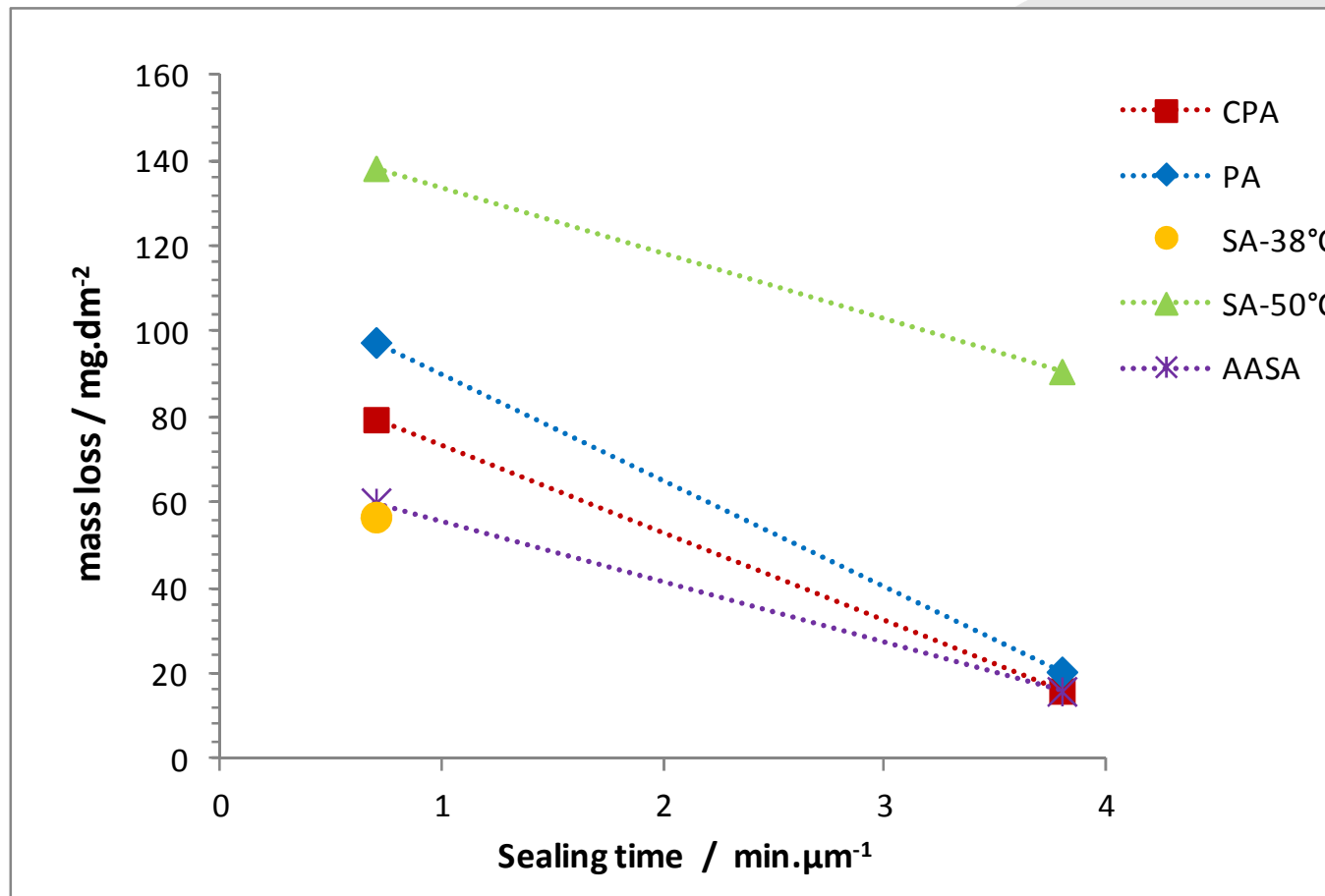


Relation between mass loss results obtained by the different immersion tests and the sealing times for the hot sealed (HS) coating types



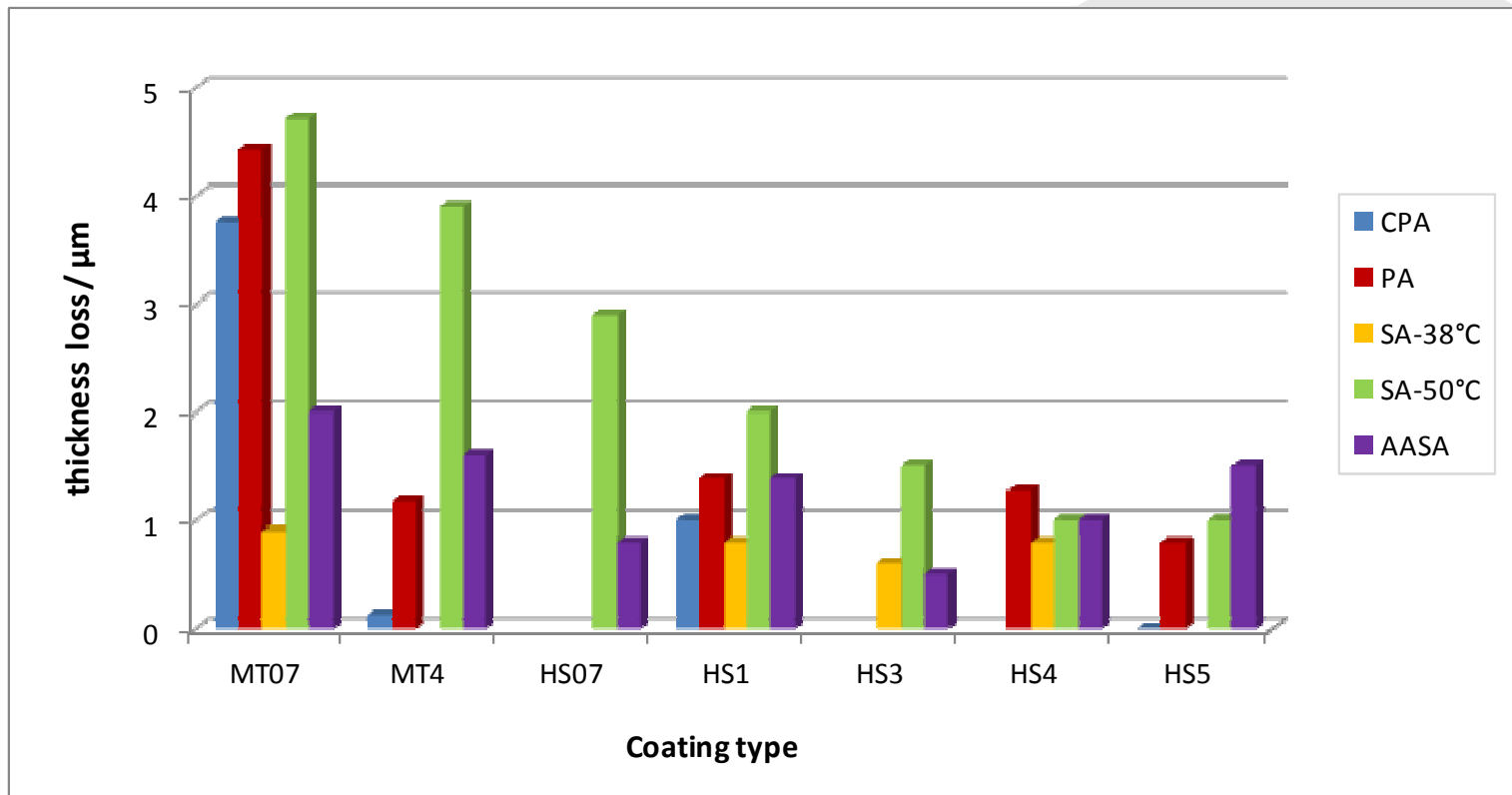
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Relation between mass loss results obtained by the different immersion tests and the sealing times for the medium temperature sealed (MT) coating types

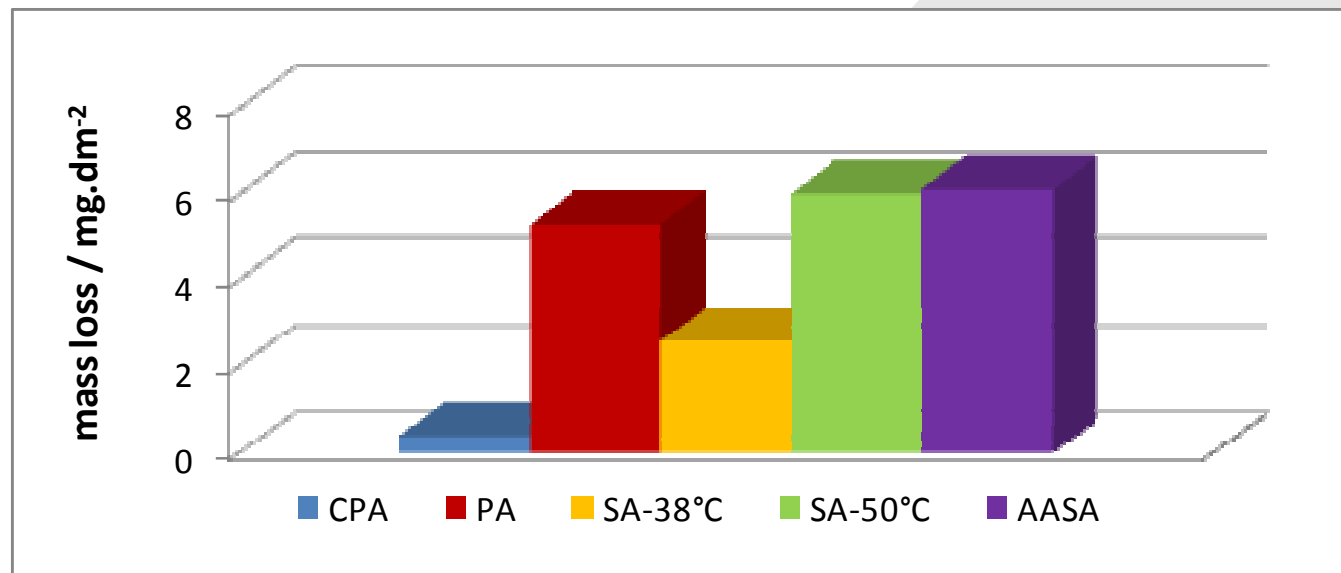


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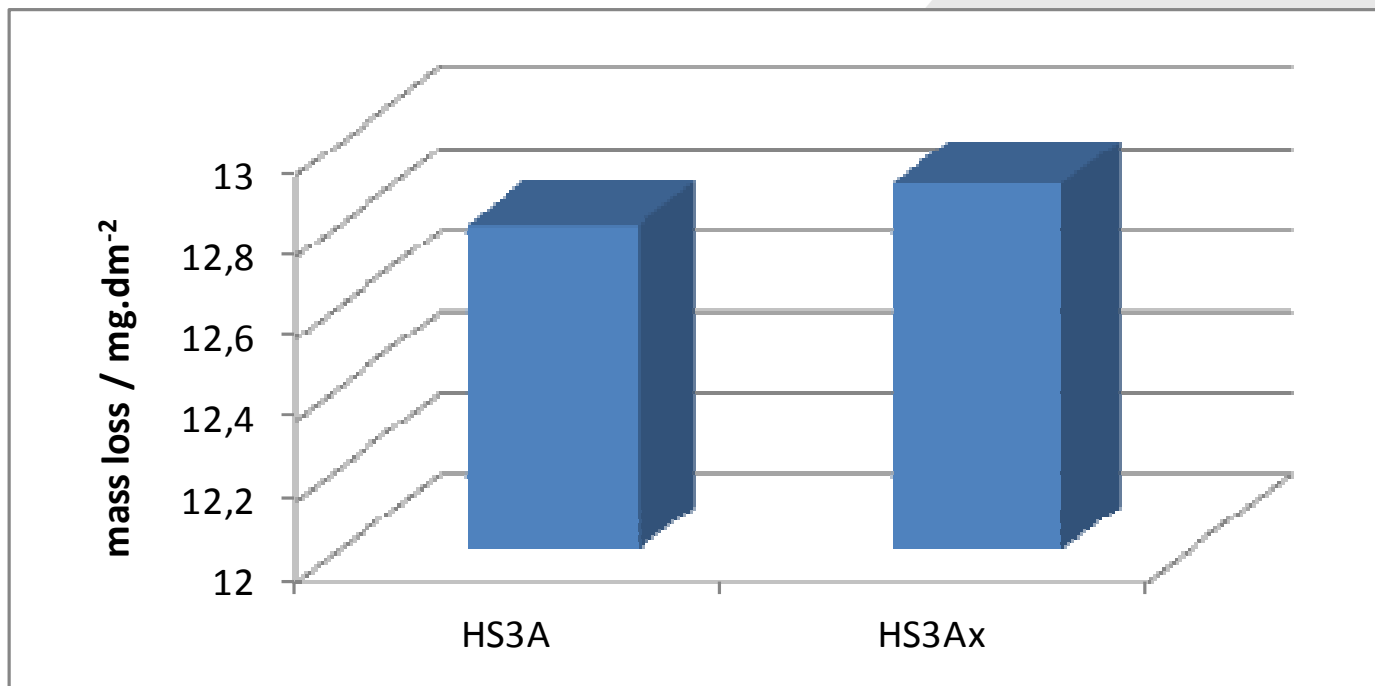
Thickness losses of the anodic coating caused by the different immersion tests by coating type



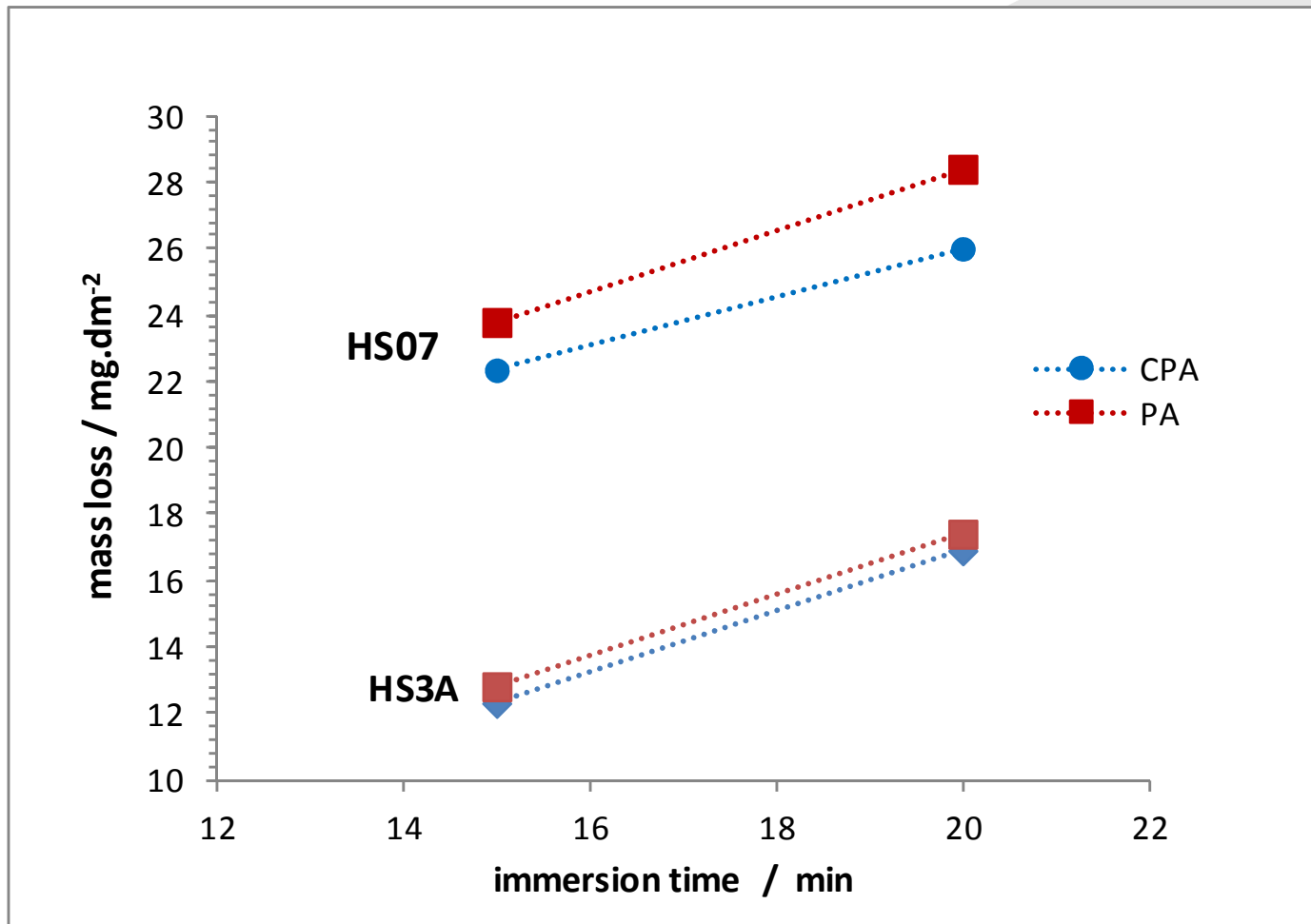
Bare aluminium mass losses obtained in each immersion test acid solution



Influence of increasing the bare aluminium area exposed on the mass loss results of the PA test (HS3Ax = HS3A grinded test specimens, with around 25% of surface uncoated)

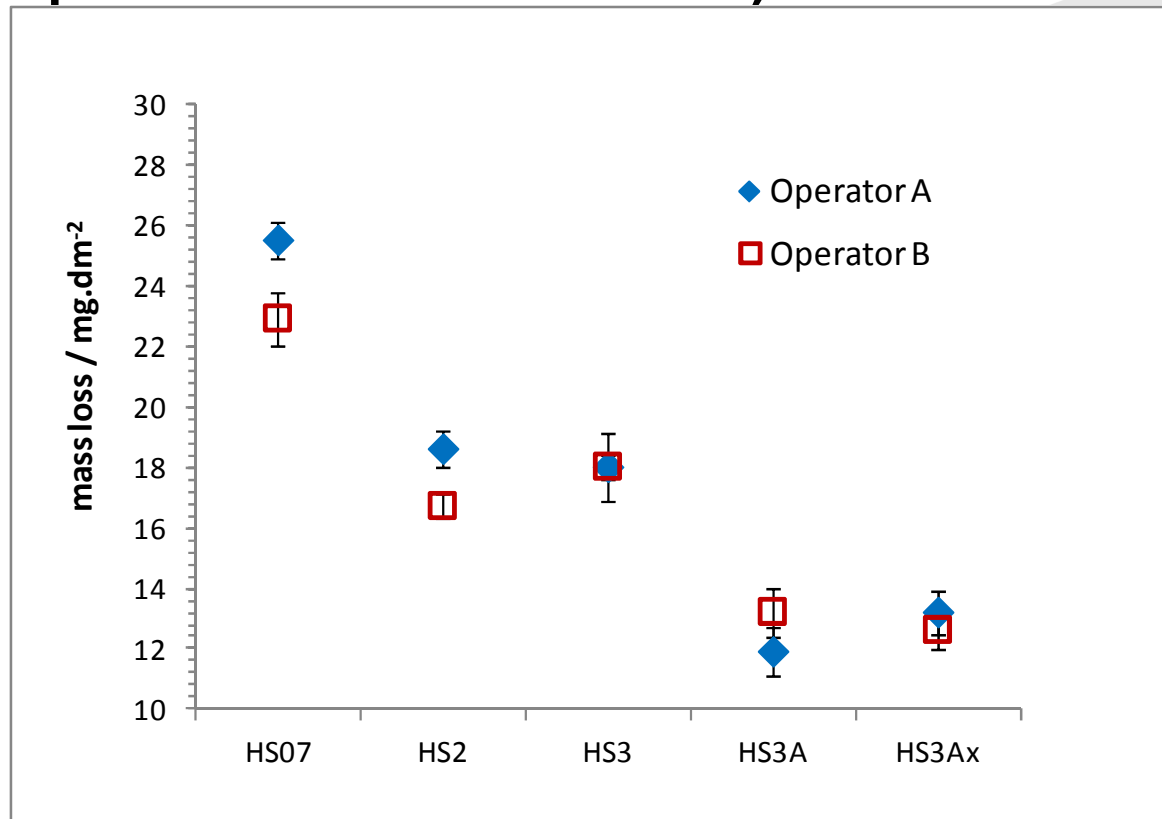


Influence of increasing the immersion time in the acid test solution on the mass loss results of PA test in comparison to CPA test



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Influence of operator on the mass loss results for the PA immersion test (data presented include the respective standard deviations)



The maximum difference between the two operators mass loss average results was 2,6 mg.dm⁻², what is inferior to the reproducibility associated to this method of 3,6 mg.dm⁻², estimated in the 2011 QUALANOD's Round Robin Inter-laboratory Test

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MAIN RESULTS LNEC RESEARCH STUDY ON SEALING TESTS

- CP vs CPA – similar results
 - base attack is about 5 mg/dm²
- S.A. 38 °C vs CPA – low attack
 - base attack about 2,6 mg/dm²
- S.A. 50 °C vs CPA – very high attack on medium temperature sealing
 - hot water sealing similar results
 - base attack about 6 mg/dm²
- A.A.S.A. vs CPA – low attack
 - base attack is larger about 6 mg/dm²
- S.A. 38 °C vs S.A. 50 °C – results are ½ of S.A. 50 °C

RRT 2011

Results of precision analysis for CPA and PA tests by anodic coating type

CPA test - EN ISO 3210 - Sealing quality by mass loss	Anodic coating type						Excluded data lab: anodic coating type
	A	B	C	E	F	G	
General mean $m / \text{mg.dm}^{-2}$	12,9	12,2	13,1	90,2	13,9	14,8	None
Repeatability std. dev. s_r	0,59	1,15	1,21	14,1	1,24	1,53	
Reproducibility std. dev. s_R	1,61	3,36	2,19	16,8	2,54	2,28	
Global repeatability std. dev.	$s_r = 0,1684 m - 1,1132$ ($R^2 \approx 1$) or $s_r = 1,1$ (if $m < 30 \text{ mg/dm}^2$)						
Global reproducibility std. dev.	$s_R = 0,1866 m - 0,0984$ ($R^2 \approx 1$) or $s_R = 2,3$ (if $m < 30 \text{ mg/dm}^2$)						
PA test - Chromium free test - Sealing quality by mass loss	Anodic coating type						Excluded data lab: anodic coating type
	A	B	C	E	F	G	
General mean $m / \text{mg.dm}^{-2}$	16,0	15,8	16,7	96,6	18,0	18,6	Lab 11: A Lab 3: B
Repeatability std. dev. s_r	1,32	1,53	0,90	13,6	1,44	2,14	
Reproducibility std. dev. s_R	3,59	3,02	3,13	16,3	4,21	4,08	
Global repeatability std. dev.	$s_r = 0,1528 m - 1,1379$ ($R^2 \approx 1$) or $s_r = 1,5$ (if $m < 30 \text{ mg/dm}^2$)						
Global reproducibility std. dev.	$s_R = 0,1592 m - 0,8884$ ($R^2 \approx 1$) or $s_R = 3,6$ (if $m < 30 \text{ mg/dm}^2$)						

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CONCLUSIONS

NEW SEALING TEST WITHOUT CROMIUM

1 - In average, the highest difference between mass loss results obtained for **CPA and PA tests** within the two experimental research programs, for the coating types with mass losses below 30 mg.dm^{-2} , is close to 5 mg.dm^{-2}

2- Therefore, a **PA test mass loss result of 30 mg.dm^{-2} , would much probably correspond to a CPA test mass loss not more than 25 mg.dm^{-2}** , which is **not an excessively too conservative acceptance** limit to assure proper sealing quality of the anodic coatings.

3- PA acid test solution attacks also the bare aluminium. But if the **uncoated surface area corresponds to 25% or less of the anodized area**, would **not be necessary to protect the uncoated surfaces** or account it, except perhaps when the mass loss result is very close to the acceptance limit.

4- **Cold sealing** specimens were **not tested**

5- **Proposal to CEN new standard** for weight mass test for sealing evaluation