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Can citric acid be used as an environmentally friendly alternative to nitric acid passivation for steel? An experimental and Life Cycle Assessment (LCA) study.

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clean space industrial days

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"Citric Acid as a Green Replacement for Steels Passivation"

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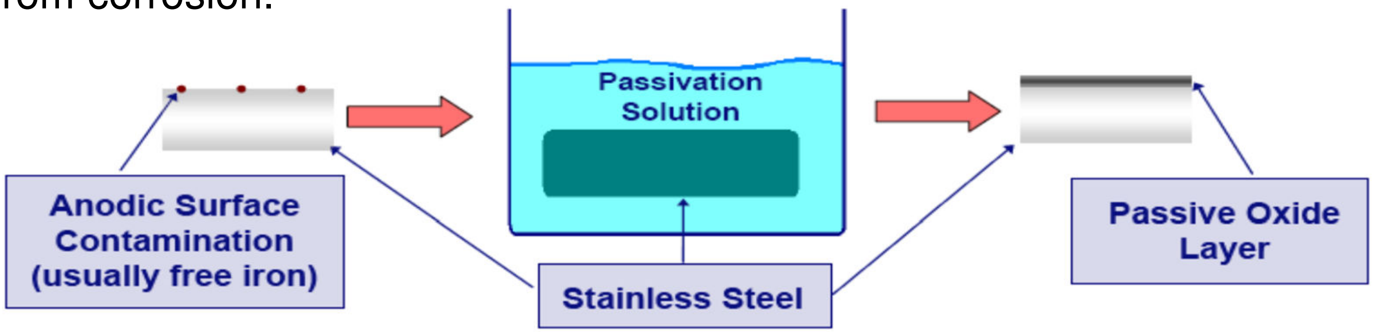
2015-2017

Stainless steels are major manufacturing materials used in spacecraft and ground support structures on applications requiring corrosion resistance:

- Containers and handling equipment of liquids and waste
- Components of propulsions systems
- Components within thermal protection systems
- Fasteners such as high strength bolts etc.

Before they are put to use stainless steel parts must first be **'passivated':**

1) To remove free iron contamination left on the surface from machining and fabrication that can result in corrosion damage
2) Forming a stable oxide film that protects the stainless steel from corrosion.



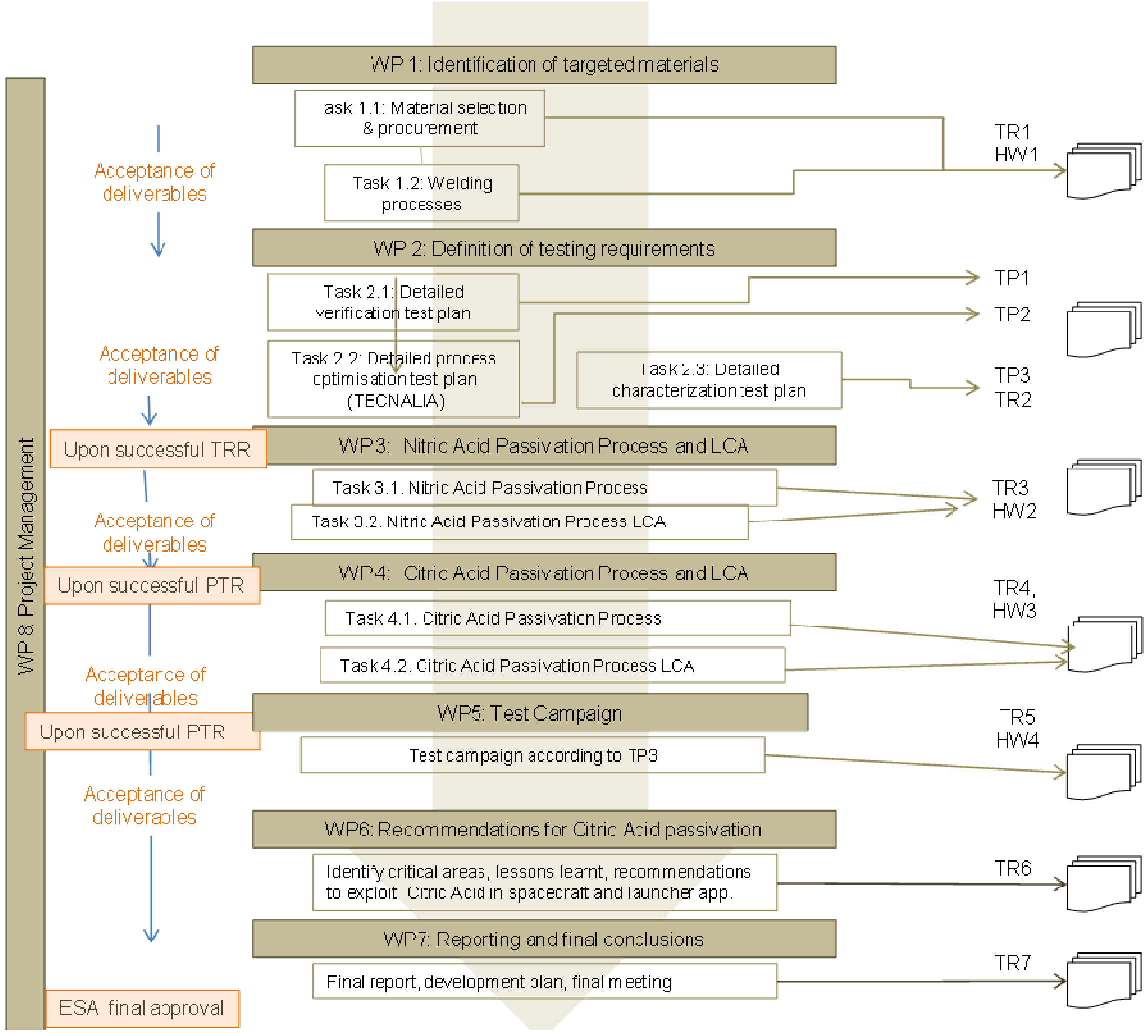
- **Nitric acid** is currently the most widely used passivating solution widely adopted in industrial applications.
- However, nitric acid has multiple **environmental, safety, and process disadvantages**.
  - Nitrogen oxides (NOx) are considered greenhouse gases and are volatile organic compounds (VOCs) that contribute to smog
  - NOx increase nitrogen concentration (leading to oxygen depletion) in water bodies
  - Poses worker health and safety issues.
  - Can remove beneficial heavy metals that give stainless steel its desirable properties
  - Nitric acid requires significant handling and disposal costs of hazardous materials.

- **Citric acid** passivation has been recently proposed as a **green replacement** for stainless steels passivation processes in different industrial sectors, including fasteners, medical devices, automotive and aerospace.
- Citric acid **is biodegradable, it is not considered a hazardous waste, it does not create toxic fumes during the passivation process and it does not remove beneficial heavy metals from the surface.**

The **objective** of the project is to evaluate the suitability of the citric acid process for replacing the nitric acid-sodium dichromate baths to passivate stainless steels used for manufacturing spacecraft and ground support structures.

Work logic

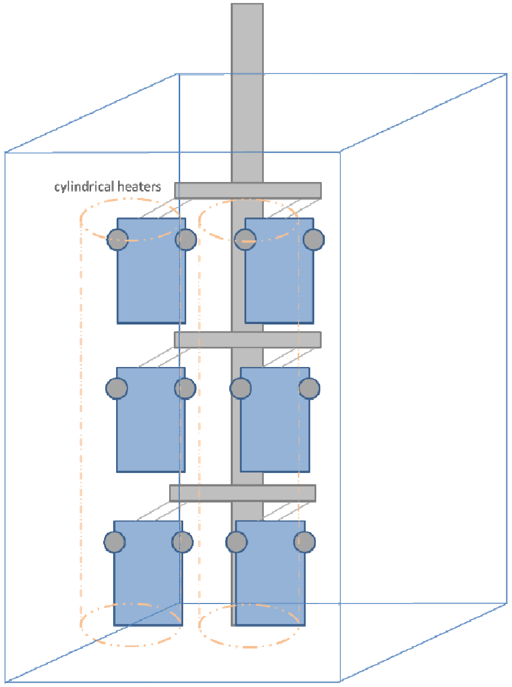
1) **Identify and procure materials (9 materials)**
2) **Identify SoA passivation processes and related standards**
3) **Identify testing methods**
4) **Verify the nitric acid passivation process by conducting two most commonly applied passivation treatments per material**
5) **Optimise the citric acid passivation process by studying different parameters (citric acid concentration, temperature and time) by means of a DoE study;**
6) **Extensive Test campaign (nitric acid and citric acid treated specimens)**
7) **Life Cycle Assessment (LCA) of nitric acid and citric acid passivation processes**
8) **Recommendations to exploit citric acid passivation**



Selected materials

Alloy	Type
AISI 304L	300 series Austenitic
AISI 316L	300 series Austenitic
AISI 321	300 series Austenitic
A 286	Prec. hardenable
PH 17-4	Prec. hardenable
PH 15-5	Prec. hardenable
PH 13-8	Prec. hardenable
AISI 440C	400 series Martensitic
CRONIDUR ® 30	Martensitic

Passivation and testing procedure



- 9 different materials
- Flat rectangular specimens 75x50x2 mm
- Apply passivation procedure (next slide)
- Blank specimens without passivation
- Response: 1) Salt spray test (x3) and 2) Ferroxyl test (x3)

VERIFICATION and OPTIMISATION campaign

✓Around 200 nitric acid passivated specimens

✓ Around 600 citric acid passivated specimens

Passivation procedure

PRE-TREATMENT

Manual acetone degreasing

Unpassivation
Steel grit blasting
Angular shape @ 6 bars

Drying
Compressed air

Alkaline degreasing
Oakite ®90
65 g/L, 80ºC, 5 min

Rinsing 1
Tap water
pH 7-10, Room T,
15 min, air bubbling

Rinsing 2
Deionised water
pH 5-7, Room T,
30 s, no stirring

Water-break test

PASSIVATION

Passivation
@[HNO3]
@Temperature
@Time
Mechanical stirring
[Fe] ≤ 2% wt.

or

Passivation
@[Citric acid]
@Temperature
@Time
Mechanical stirring
[Fe] ≤ 2% wt.

Rinsing 3
Tap water
pH 5-9, Room T,
15 min, air bubbling

Rinsing 4
Deionised water
pH 5-7, Room T,
30 s, no stirring

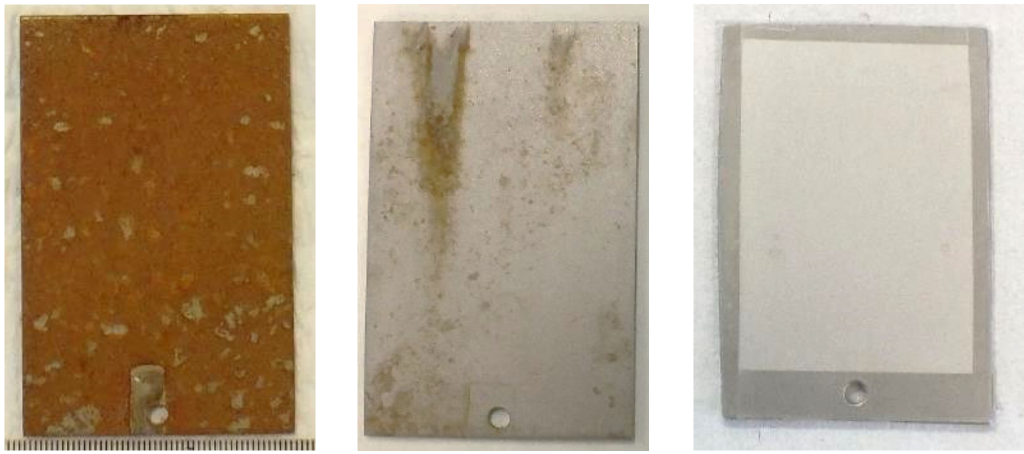
Drying
Cold blow air

Storage
Controlled aerated atmosphere

Testing effectiveness of passivation

Salt Spray test (ASTM B117)

- Passivation effectiveness assessment as per ASTM A967 and AMS2700C
- 48 hours of exposure (2 hours are required as minimum in the ASTM A967/A967M-13 standard)
- 2 hours of exposure for AISI 440C and Cronidur30 (very sensitive to corrosion)
- The rust or staining after completion of the test shall be attributable to the presence of free iron particles embedded on the surface (insufficient passivation)



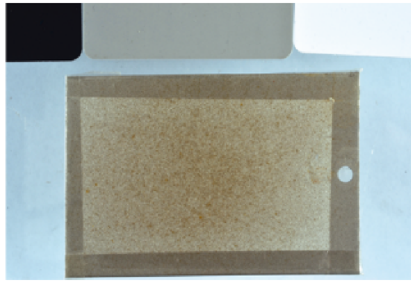
316L Non-passivated (blank) | 316L Insufficiently passivated | 316L Well passivated

Testing effectiveness of passivation

<u>Salt Spray test</u> (ASTM B117)

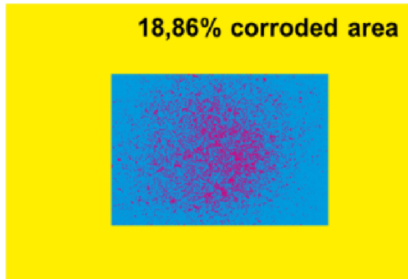
- The amount of rust or staining produced on the surface of the specimens (% of corroded area) was quantified using Image analysis software
- In principle, at least for the austenitic steels, it was expected that the nitric acid passivated specimens should not exhibit any rust or staining attributable to the presence of free iron particles
- Blank unpassivated specimens should give a positive response of a minimum of 50 % of stained surface

1) Initial photograph



2) Calibration of colour

3) Crop region of interest and apply grey scale



4) Apply thresold (magenta) and sum-up thresold area

Testing effectiveness of passivation

Ferroxyl test

- Passivation effectiveness assessment as per ASTM A967 and AMS2700C (not recommended for martensitic grades)
- The Ferroxyl test solution was swabbed on the surface of each of the test specimens. The formation of a dark blue colour within 30 s denotes the presence of metallic iron.
- The blue staining after completion of the test shall be attributable to the presence of free iron particles embedded on the surface (insufficient passivation)

316L Non-passivated (blank)

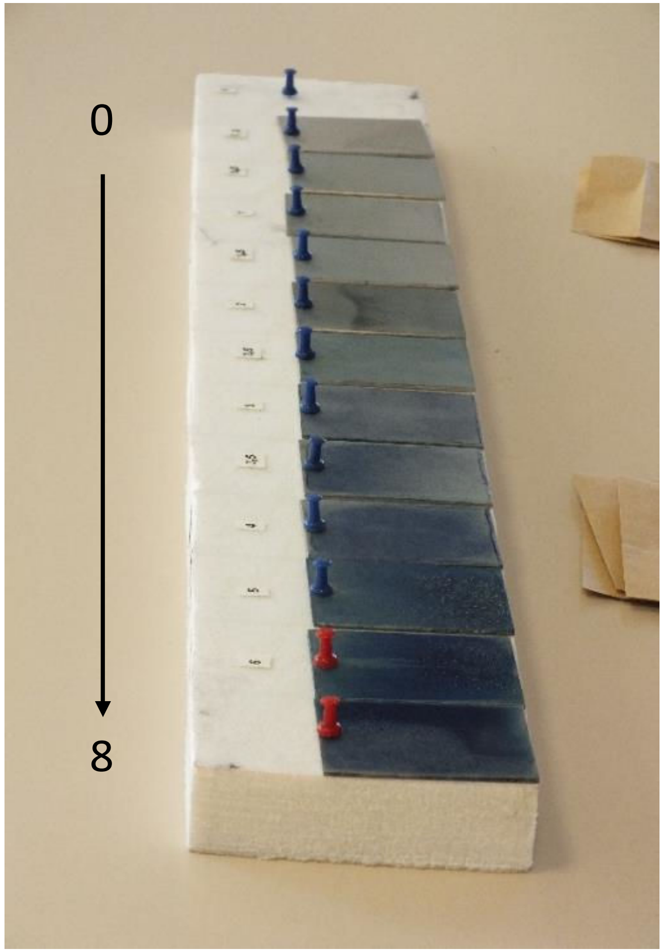
316L Insufficiently passivated

316L Well passivated

Testing effectiveness of passivation

Ferroxyl test

- The dark blue staining produced on the surface of the specimens was quantified (after 1-3 days of testing) using a coloration grade scale to get a grade (from 0 to 8) of the surface that has been stained
- In principle, at least for the austenitic steels, it was expected that the nitric acid passivated specimens should not exhibit any blue staining attributable to the presence of free iron particles
- Blank unpassivated specimens should give a positive response of a minimum score of 7



Nitric acid passivation verification test matrix

Austenitic grades (AISI 304L, AISI 316L, AISI 321)				
Treatment	**[HNO3]**	**T**	**time**	**Selection logic**
1)	35% vol HNO_3 67%wt	25ºC	45 min	Compliant with method Nitric 2 (ASTM A 967), with method F (ASTM-380) and with method Nitric 6 (AMS 2700C).
2)	25% vol HNO_3 67%wt	55ºC	30 min	Compliant with method Nitric 3 (ASTM A 967), with method F (ASTM A380) and with method Nitric 7 (AMS 2700C).

PH and martensitic grades (A286, 15-5 PH, 17-4 PH, 13-8 PH, AISI 440C and C30)				
Treatment	**[HNO3]**	**T**	**time**	**Selection logic**
1)	50% vol HNO3 67%wt	50ºC	30 min	Compliant with method Nitric 4 (ASTM A 967), with method H (ASTM A380) and with method Nitric 8 (AMS 2700C).
2)	25% vol HNO3 67%wt + 2.5%wt sodium dichrom.	50ºC	30 min	Compliant with method Nitric 1 (ASTM A 967), with method I (ASTM A380) and with method Nitric 2 (AMS 2700C).
3)	50% vol HNO3 67% wt	50ºC	60 min	Slightly forcing time. Compliant with method Nitric 4 (ASTM A 967).
4)	50% vol HNO3 67% wt	64ºC	30 min	Slightly forcing temperature. Out of standards.

Response	Units
Salt Spray Test: Determination of the total corroded area (%) after the test	% corroded area
Ferroxyl Test: Determination of the coloration grade (specific grade in a scale from 0 to 8) after the test	Coloration grade (from 0 to 8)

Summary of results for nitric acid passivation

- **Austenitic grades:**
  - **Best treatments** operated at lower concentration, higher temperature and lower processing time conditions, i.e. **[25% vol HNO_3 c.@55ºC@30 min]**
  - The salt spray corrosion response was in all cases lower than 1% of corroded area
  - Ferroxyl response was as low as 1 (in the scale going from 0 to 8)
- **PH grades:**
  - Treatment #3 **[50% vol. HNO_3 c.@50ºC@60 min]** was selected as the best one to nitric acid passivate **15-5 PH, 17-4 PH and 13-8 PH** grades
  - The salt spray corrosion response was in both cases lower than 3% of corroded area and Ferroxyl response was between 5 and 6
  - Treatment #4 **[50% vol. HNO3 c.@64ºC@30 min]** was selected as the best one for **A286**
- **Martensitic grades:**
  - Treatment #4 **[50% vol. HNO3 c.@64ºC@30 min]** gave the best results in Salt Spray test (20,37% corroded area) for AISI 440C
  - Treatment #1 **[50% vol. HNO3 c.@50ºC@30 min]** gave the best results in Salt Spray test (8,63% corroded area) for Cronidur®30

Nitric acid passivation selected optimum parameters

Material	Treatment #	[Nitric citric] *	Temp. (ºC)	Time (min)	Salt Spray (%)*	Ferroxyl Grade (0 to 8)*
AISI 304L	2	25% vol HNO_3 c.	55ºC	30 min	0,37%	1
AISI 316L	2	25% vol HNO_3 c.	55ºC	30 min	0,82%	1
AISI 321	2	25% vol HNO_3 c.	55ºC	30 min	0,82%	1
15-5 PH	3	50% vol HNO_3 c.	50ºC	60 min	2,80%	5,67
17-4 PH	3	50% vol HNO_3 c.	50ºC	60 min	1,03%	5,33
13-8 PH	3	50% vol HNO_3 c.	50ºC	60 min	0,03%	-
AISI A286	4	50% vol HNO_3 c.	64ºC	30 min	1,20%	3,16
AISI 440C	4	50% vol HNO3 c.	64ºC	30 min	20,37%	-
C®30	1	50% vol HNO_3 c.	50ºC	30 min	8,63%	-

Results for nitric acid passivation. Some examples.

AISI 304L

SALT SPRAY 48h (Photo after test and image analysis)

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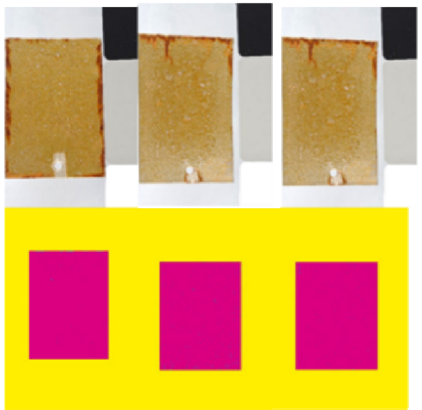
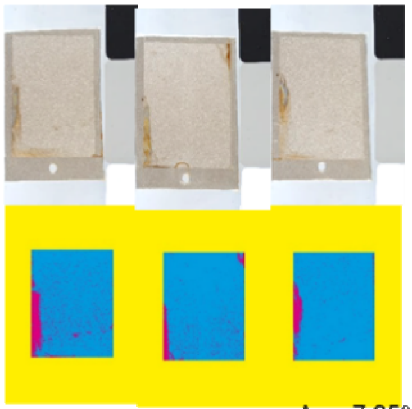


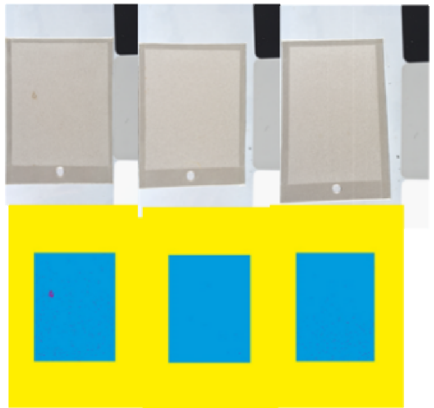
Avg. 99,57%

HNO3 c. 35% vol.@25ºC@45'



Avg. 7.95%

HNO3 c. 25% vol.@55ºC@30'



Avg. 0.37%

FERROXYL (Photo after 1 hour of testing)

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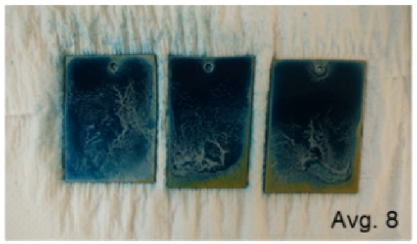
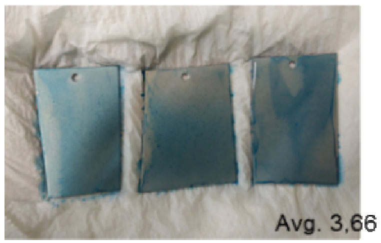


HNO3 c. 35% vol.@25ºC@45'



HNO3 c. 25% vol.@55ºC@30'

Results for nitric acid passivation. Some examples.

15-5 PH

SALT SPRAY 48h (Photo after test and image analysis)

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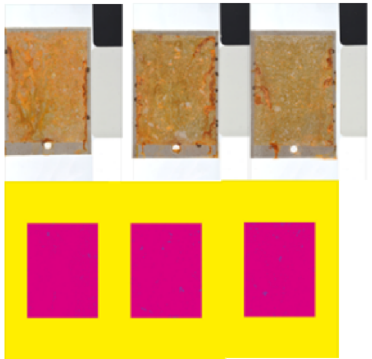
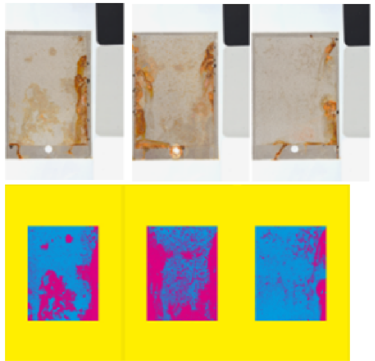


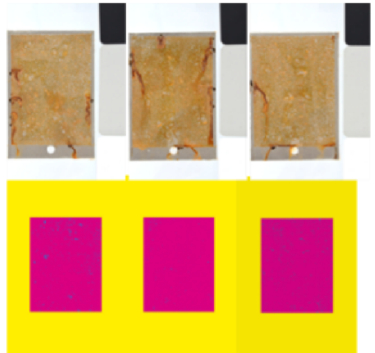
Avg. 99,28%

HNO3 c. 55% vol.@50ºC@30' (#1)



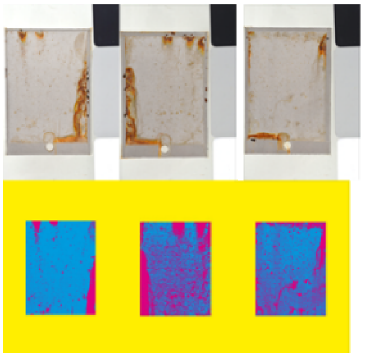
Avg. 39,46%

HNO3 c. 25% vol.+2,5% wt. Na dichromate @55ºC@30' (#2)



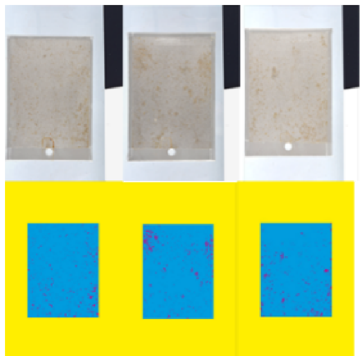
Avg. 98,15%

HNO3 c. 55% vol.@50ºC@60' (#3)



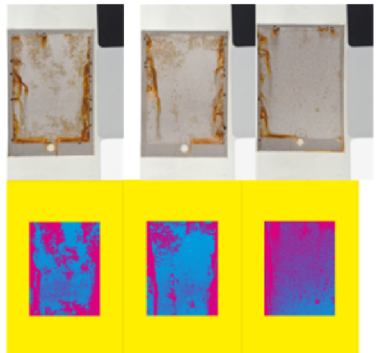
Avg. 32,07%

HNO3 c. 55% vol.@50ºC@30' (#3Rep)



Avg. 2,80%

HNO3 c. 55% vol.@64ºC@30' (4#)



Avg. 47,92%

Results for nitric acid passivation. Some examples.

CRONIDUR®30

SALT SPRAY 48h (Photo after test and image analysis)

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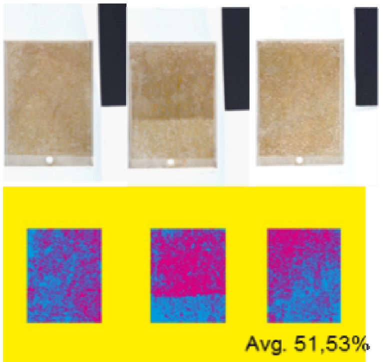
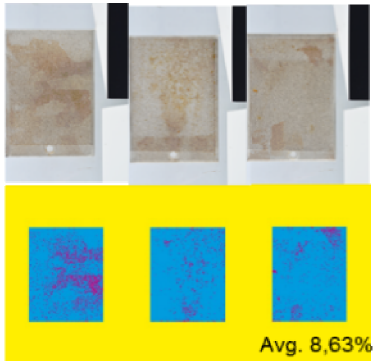
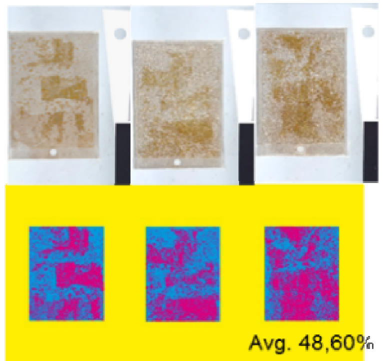


HNO3 c. 55% vol.@50ºC@30' (#1)

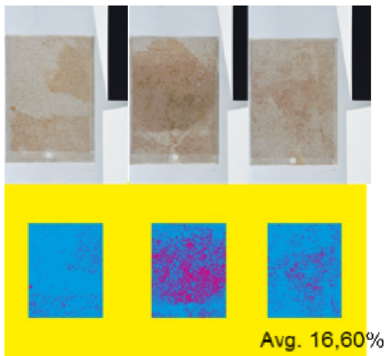


HNO3 c. 55% vol.@50ºC@60' (#3)

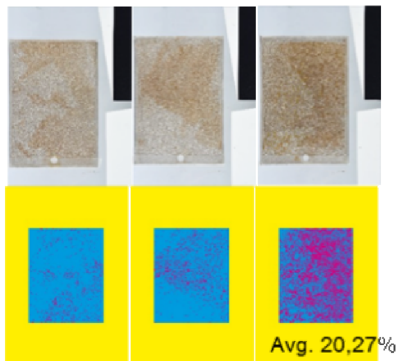


SALT SPRAY 48h (Photo after test and image analysis)

HNO3 c. 55% vol.@50ºC@60' (#3)



HNO3 c. 55% vol.@64ºC@30' (#4)



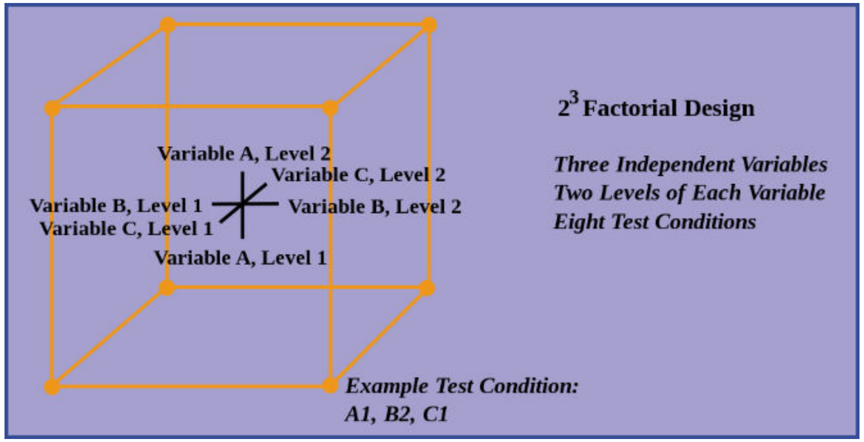
Citric acid passivation optimisation test matrix

2^3 factorial DoE + estimation of the variances at the central point

Austenitic grades (AISI 304L, AISI 316L, AISI 321)		
Factors	Lower limit	Upper limit
Citric acid concentration	4 wt %	10 wt %
Temperature	25ºC	85ºC
Treatment time	15 min	150 min

PH and martensitic grades (A286, 15-5 PH, 17-4 PH, 13-8 PH, AISI 440C and C30)		
Factors	Lower limit	Upper limit
Citric acid concentration	4% wt	10% wt
Temperature	25ºC	85ºC
Treatment time	15 min	90 min

Response	Units
Salt Spray Test: Determination of the total corroded area (%) after the test	% corroded area
Ferroxyl Test: Determination of the coloration grade (specific grade in a scale from 0 to 8) after the test	Coloration grade (from 0 to 8)



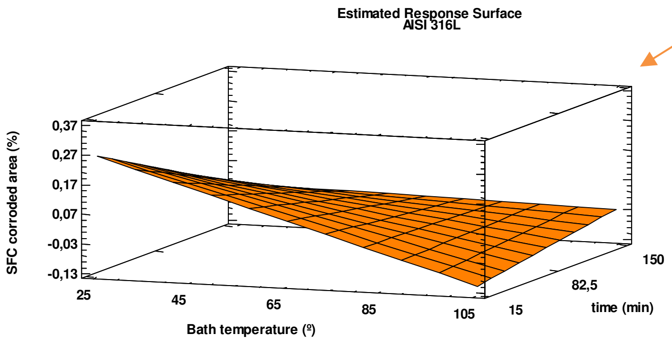
- Analyzes multiple test parameters simultaneously
- Exposes interactions between variables
- Delivers optimized combination of variables

Citric acid passivation optimisation test matrix

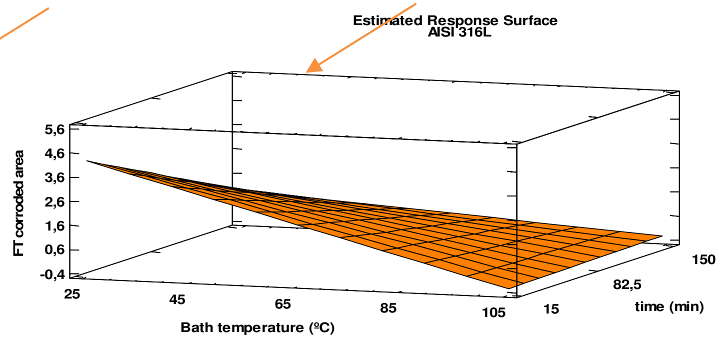
2^3 factorial DoE + estimation of the variances at the central point

Example 316L

Run #	Design factors			Responses							
	Citric Acid conc. (%)	Bath Temp. (ºC)	Time (min)	SST corroded area (%)				Ferroxyl grade (0 to 8)			
				CNS1	CNS2	CNS3	Average	F-1	F-2	F-3	Average
1	10	25	15	18,02	18,86	0,24	**6,37**	5	6	5	**5,33**
2	10	85	15	0	0	0	**0,00**	1	1	1	**1**
3	4	85	15	0	0	0	**0,00**	1	1	1	**1**
4	7	55	82,5	0	0	0	**0,00**	1	0,5	1	**0,83**
5	10	25	150	0,04	0,01	0,02	**0,01**	0,5	1	1,5	**1**
6	4	25	150	0,08	0,06	0,02	**0,03**	1	1,5	1,5	**1,33**
7	4	25	15	1,11	17,0	0,32	**5,77**	4	3,5	3	**3,5**
8	10	85	150	0	0	0	**0,00**	0,3	0,3	0,3	**0,3**
9	7	55	82,5	0	0,01	0,02	**0,01**	1	1	0,75	**0,91**
10	4	85	150	0	0	0	**0,00**	0,3	0,3	0,3	**0,3**
11	7	55	82,5	0	0	0	**0,00**	1	1,5	1	**1,33**



Model for salt spray response



Model for Ferroxyl response

Citric acid passivation DoE models and optimum process parameters

Material	**DoE Model** (SST Corroded area %)	**Optimised process parameters** Citric acid (wt%)	Temp(ºC)	Time (min)	**Predicted value** (SST Corroded area %)	**Actual value** (SST Corroded area %)
AISI 304L	Does not fit to a statistical model. All experimental runs achieved the target 0% corroded area.	4%	85ºC	15´	0%	0%
AISI 316L	*$SST_{corroded\ area}$ (%) = 0,419 - 0,005 · Bath Temperature - 0,003 · time + 0,00003 · (Bath temperature x time)*	4%	85ºC	150´	-0.02±0.05%	0%
AISI 321	Does not fit to a statistical model. All experimental runs achieved the target 0% corroded area.	4%	85ºC	150´	0%	0%
15-5 PH	*$SST_{corroded\ area}$ (%) = 176,79 - 3,47 · Citric acid concentration – 3,37 · Bath temperature - 0,32 · time + 0,02 · (Bath temperature)^2*	7%	85ºC	90´	-1.78±13.78%	0,33%
17-4 PH	*$SST_{corroded\ area}$ (%) = 38,10 – 0,005· (Bath temperature x time)*	4%	85ºC	90´	-1.22±12.70%	0,66%
13-8 PH	-	7%	85ºC	90´	-	0,03%
AISI A286	*$SST_{corroded\ area}$ (%) = -0,24 + 0,25 · Bath temperature - 0,016 · (Citric Acid Concentration x Bath temperature) - 0,001 · (Bath temperature x time)*	10%	85ºC	90´	-3.55±4.23%	0,33%
AISI 440C	*$SST_{corroded\ area}$ (%) = 114,89 - Bath Temperature – 1,91 · time + 0,018· (time)^2*	4%	85ºC	60´	-18.53±4.53%	6,00%
C®30	*$SST_{corroded\ area}$ (%) = 13,16 - 0,38 · time - 0,024 · (Citric Acid Concentration x Bath Temperature) + 0,12 · (Citric Acid Concentration)^2 + 0,004 (time)^2*	7%	85ºC	60´	-4.16±2.4%	0,77%

Citric acid passivation DoE models and optimum process parameters

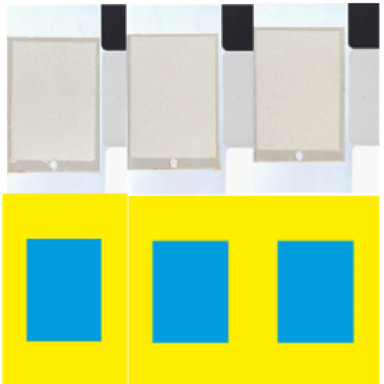
Material	DoE Model (Ferroxyl grade from 0 to 8)	Optimised process parameters			Predicted value (Ferroxyl grade from 0 to 8)	Actual value (Ferroxyl grade from 0 to 8)
		Citric acid (wt%)	Temp (ºC)	Time (min)		
AISI 304L	*Ferroxyl grade = 2,701 + 0,330 · Citric Acid Concentration - 0,023 · time - 0,007 · (Citric Acid Concentration x Bath temperature) + 0,0003 · (Bath temperature x time)*	4%	85ºC	15´	0.45±0.82	1,83
AISI 316L	*Ferroxyl grade = 6,127 - 0,062 · Bath Temperature - 0,032 · time + 0,0003 · (Bath temperature x time)*	4%	85ºC	150´	0.11±0.78	0,3
AISI 321	*Ferroxyl grade = 4,785 - 0,035 · Bath Temperature - 0,01 · time*	4%	85ºC	150´	0.22±0.65	0,83
15-5 PH	*Ferroxyl Grade = 6,30 - 0,001· (Bath temperature x time) + 0,0004 · (time)^2*	7%	85ºC	90´	0.86±1.41	3,17
17-4 PH	*Ferroxyl Grade = 10,68 – 0,008 · x Bath temperature – 0.0004 · (Bath temperature x time)*	4%	85ºC	90´	1.03 ± 1.2	1,66
13-8 PH	-	7%	85ºC	90´	-	-
AISI A286	*Ferroxyl grade = 11,40 - 0,70 · Citric Acid Conc. - 0,02 · Bath temperature - 0,07 · time + 0,006 · (Citric Acid Concentration x time)*	10%	85ºC	90´	1.91±0.71	1,83
AISI 440C	-	4%	85ºC	60´	-	-
C®30	-	7%	85ºC	60´	-	-

Results for citric acid passivation. Some examples.

AISI 304L

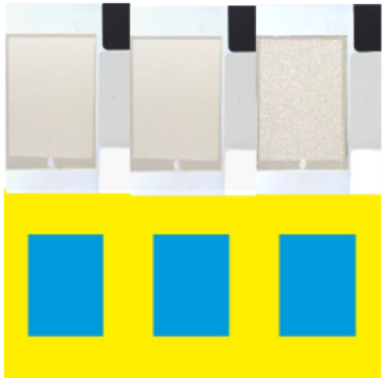
SALT SPRAY 48h (Photo after test and image analysis)

10%wt C.A.@85ºC@150' (#8-Best)



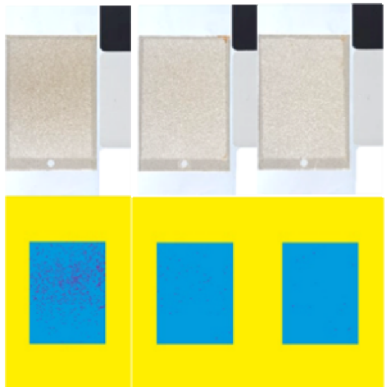
Avg. 0.00%

7%wt C.A.@55ºC@82,5' (#4-Med)



Avg. 0.00%

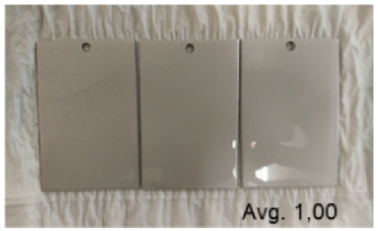
10%wt C.A.@25ºC@15' (#1-Worst)



Avg. 2.16%

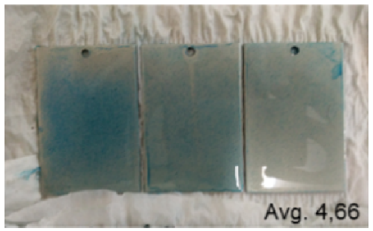
FERROXYL (Photo after 1 hour of testing)

10%wt C.A.@85ºC@150' (#8-Best)



7%wt C.A.@55ºC@82,5' (#4-Med)

10%wt C.A.@25ºC@15' (#1-Worst)

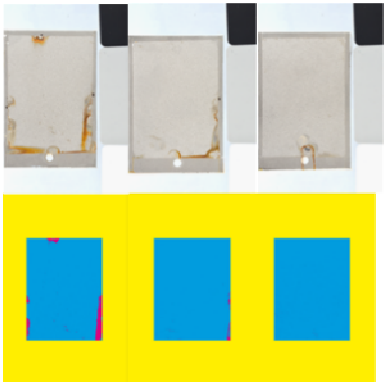


Results for citric acid passivation. Some examples.

15-5 PH

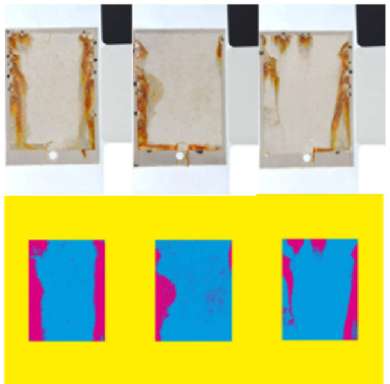
SALT SPRAY 48h (Photo after test and image analysis)

10%wt C.A.@85ºC@90' (#5-Best)



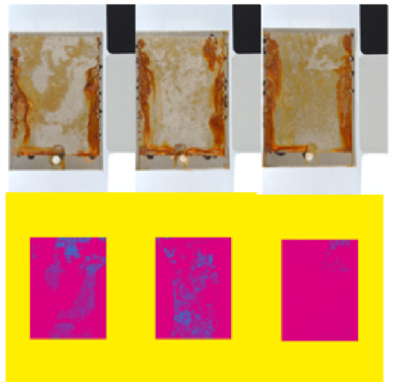
Avg. 1.56%

7%wt C.A.@55ºC@52,5' (#3-Med)



Avg. 20.87%

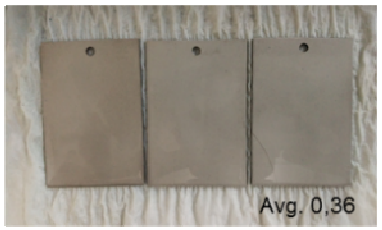
4%wt C.A.@25ºC@15' (#9-Worst)



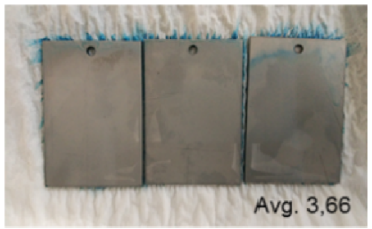
Avg. 92,98%

FERROXYL (Photo after 1 hour of testing)

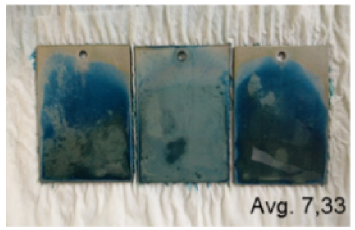
10%wt C.A.@85ºC@90' (#5-Best)



7%wt C.A.@55ºC@52,5' (#3-Med)



4%wt C.A.@25ºC@15' (#9-Worst)

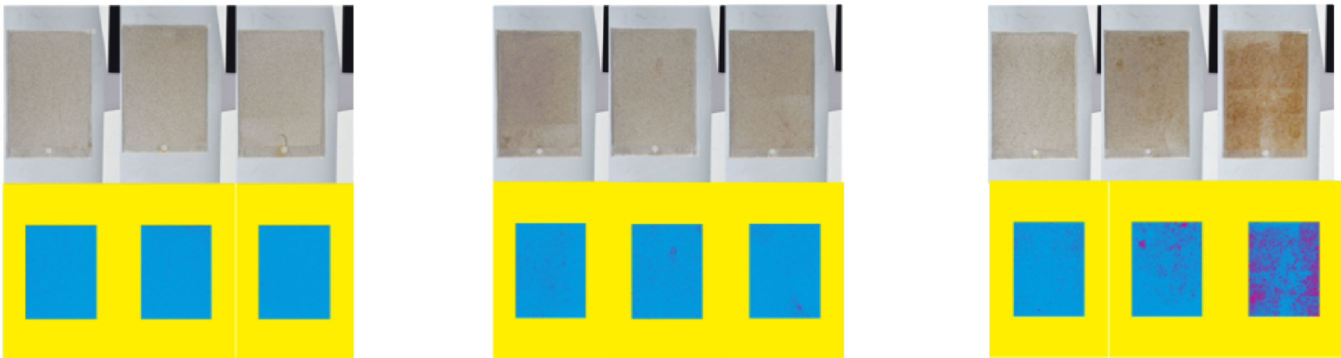


Results for citric acid passivation. Some examples.

Cronidur® 30

SALT SPRAY 2h (Photo after test and image analysis)

10%wt C.A.@85ºC@15' (#2-Best) | 7%wt C.A.@55ºC@52,5' (#9-Med) | 10%wt C.A.@25ºC@15' (#4-Worst)



Avg. 1,23% | Avg. 2,60% | Avg. 13,77%

Assessment of results and industrial conditions

- Salt spray and Ferroxyl responses were **better for citric acid passivation** than for citric acid passivation for all studied grades.
- However the optimised process conditions for citric acid passivation led in general to high temperatures and long processing times (i.e. **85ºC @ 90-150 min** depending on the material) since the objective was to minimise as much as possible the corrosion response.
- A further analysis of the citric acid passivation results was conducted trying to assess which parameters could be practically implemented at an industrial scale. To do so, a “realistic” temperature to work at industrial scale was arbitrarily defined at 60ºC.
- The results showed that, **promisingly, salt spray responses near to 0% corroded area or at least under ≤10% of corroded area were achievable for all the materials working at 60ºC.** Processing time could be also reduced in some of the materials keeping low corrosion responses.

Test Campaign

The necessary samples to be tested in the Characterisation Test Campaign were nitric acid and citric acid passivated applying the conditions selected as optimum for each material

TEST campaign

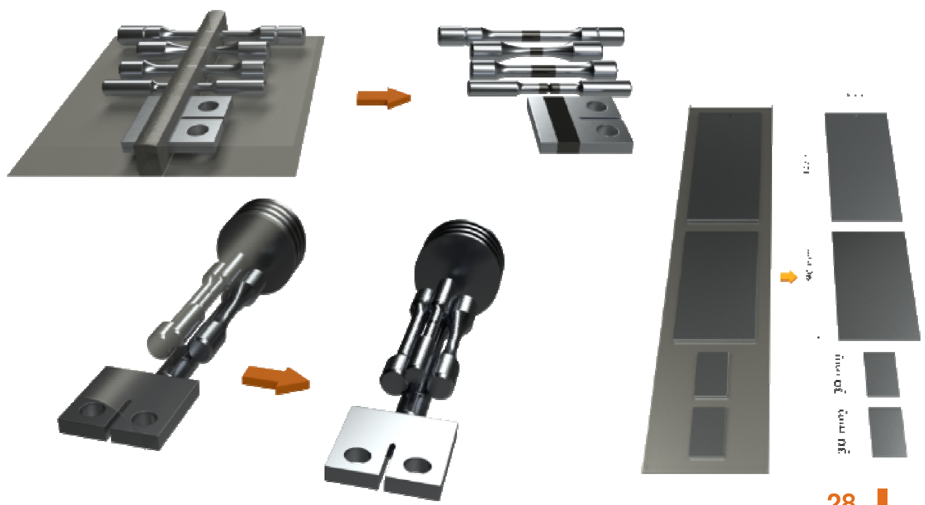
✓ **Around 1250 nitric and citric acid passivated specimens**

MECHANICAL and MICROESTRUCTURAL CHARACTERIZATION
Tensile testing
Hardness and microhardness testing
Microstructural characterisation
Fatigue testing(R=0,1 and R=-1)
Fatigue crack propagation (R=0,1 and R=1)

CORROSION CHARACTERIZATION
General corrosion testing.
Athmospheric corrosion testing
SCC testing
Hydrogen embrittlement testing
Electrochemical testing

CHEMICAL CHARACTERIZATION

XPS chemical compositon
Hydrogen content



Test Campaign

	Standard	#material	Condition	P	NA	CA	W	NAW	CAW	No. specimens/ref	Samples total
Chemical composition	XPS	9	2		1	1					
Hydrogen content		9	3	1	1	1				3	81
Tensile testing	EN ISO 6892 1	6	6	1	*	1	1	1	1	3 (* corresponds 2 samples)	102
Tensile testing (Cronidur, 440C, A286)	EN ISO 6892-1	3	3	1	1	1				3	27
Hardness	EN ISO 6506-1, ISO6508-1	6	6	1	1	1	1	1	1	1	36
Hardness (Cronidur, 440C, A286)	EN ISO 6506-1, ISO6508-1	3	3	1	1	1				1	9
Microhardness (no welded)	EN ISO 6507-1	9	2		1	1				1	18
Microhardness (welded)	EN ISO 9015-1 & EN ISO 9015-2	9	2					1	1	1	18
Microstructural characterisation	Internal procedure	6	6	1	1	1	1	1	1	1	36
Microstructural characterisation (Cronidur, 440C, A286)	Internal procedure	3	3	1	1	1				1	9
General corrosion testing (salt fog testing)	EN ISO 9227	9	6	1	1	1	1	1	1	2	108
Atmospheric corrosion testing		9	6	1	1	1	1	1	1	2	108
SCC testing (AISI304L, AISI316L, AISI321)	ECSS-Q-ST-70-37C	3	2					1	1	6	36
SCC testing (PH15-5, PH17-4, PH13-8)	ECSS Q ST 70 37C	3	2					1	1	6	36
SCC testing (A286)	ECSS-Q-ST-70-37C	1	2		1	1				6	12
SCC testing (Cronidur, 440C)	ECSS-Q-ST-70-37C	2	2		1	1				6	24
Hydrogen embrittlement	ASTM F519-13	6	3			1		1	1	3	60
Hydrogen embrittlement (Cronidur, 440C, A286)	ASTM F519-13	3	3	1	1	1				3	27
Electrochemical	ASTM G61	6	6	1	1	1	1	1	1	1	36
Electrochemical (cronidur, 440C, A286)	ASTM G61	3	3	1	1	1				1	9
Fatigue testing (2 R values)	ASTM E466	6	3			1		1	1	12	432
Fatigue testing (2 R values) (Cronidur, 440C, A286)	ASTM E466	1	3	1	1	1				12	36
Fatigue crack propagation (2 R values)	ASTM E647	6	3			1		1	1	2	72
Fatigue crack propagation (2 R values) (cronidur, 440C, A286)	ASTM E647	3	3	1	1	1				2	36
										Total:	1251

Tests in progress

Test Campaign

	Standard	#material	Condition	P	NA	CA	W	NAW	CAW	No. specimens/ref	Samples total
Chemical composition	XPS	9	2		1	1					
Hydrogen content		9	3	1	1	1				3	81
Tensile testing	EN ISO 6892-1	6	6	1	*	1	1	1	1	3 (* corresponds 2 samples)	102
Tensile testing (Cronidur, 440C, A286)	EN ISO 6892-1	3	3	1	1	1				3	27
Hardness	EN ISO 6506-1. ISO6508-1	6	6	1	1	1	1	1	1	1	36
Hardness (Cronidur, 440C, A286)	EN ISO 6506-1. ISO6508-1	3	3	1	1	1				1	9
Microhardness (no welded)	EN ISO 6507-1	9	2		1	1				1	18
Microhardness (welded)	EN ISO 9015-1 & EN ISO 9015-2	9	2					1	1	1	18
Microstructural characterisation	Internal procedure	6	6	1	1	1	1	1	1	1	36
Microstructural characterisation (Cronidur, 440C, A286)	Internal procedure	3	3	1	1	1				1	9
General corrosion testing (salt fog testing)	EN ISO 9227	9	6	1	1	1	1	1	1	2	108
Atmospheric corrosion testing		9	6	1	1	1	1	1	1	2	108
SCC testing (AISI304L, AISI316L, AISI321)	ECSS-Q-ST-70-37C	3	2					1	1	6	36
SCC testing (PH15-5, PH17-4, PH13-8)	ECSS-Q-ST-70-37C	3	2					1	1	6	36
SCC testing (A286)	ECSS-Q-ST-70-37C	1	2		1	1				6	12
SCC testing (Cronidur, 440C)	ECSS-Q-ST-70-37C	2	2		1	1				6	24
Hydrogen embrittlement	ASTM F519-13	6	3			1		1	1	3	60
Hydrogen embrittlement (Cronidur, 440C, A286)	ASTM F519-13	3	3	1	1	1				3	27
Electrochemical	ASTM G61	6	6	1	1	1	1	1	1	1	36
Electrochemical (cronidur, 440C, A286)	ASTM G61	3	3	1	1	1				1	9
Fatigue testing (2 R values)	ASTM E466	6	3			1		1	1	12	432
Fatigue testing (2 R values) (Cronidur, 440C, A286)	ASTM E466	1	3	1	1	1				12	36
Fatigue crack propagation (2 R values)	ASTM E647	6	3			1		1	1	2	72
Fatigue crack propagation (2 R values) (cronidur, 440C, A286)	ASTM E647	3	3	1	1	1				2	36
										Total:	1251

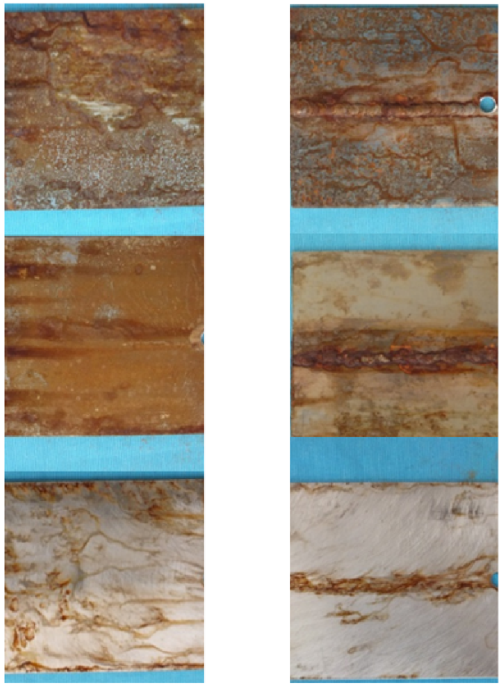
Overall Similar performance nitric vs. citric acid

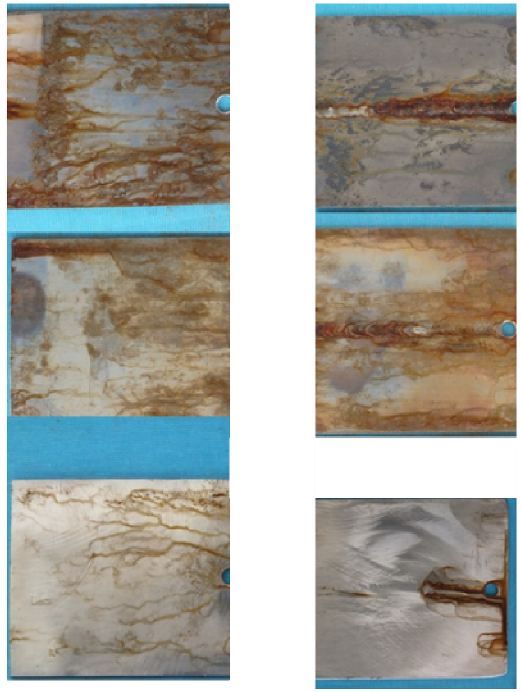
Citric acid better than nitric acid

Results after 168 hours of SST testing

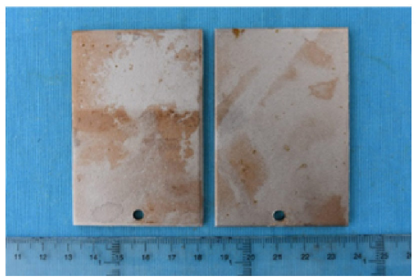
Nitric Acid pasivated | Citric Acid pasivated

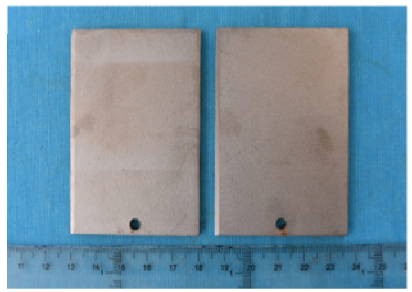
- 15-5
- 17-4
- 13-8





- C30





Hydrogen embrittlement testing

Nitric acid passivated AISI 440C specimens failed the test while those citric acid passivated passed it.

Reference	7	7N	7C
Spec. 1 (MPa)	1826		
Spec. 2(MPa)	1999		
Spec 3 (MPa)	1361		
NFS (MPa)	1728,7		
Stress applied (MPa)	1296,5		
Time (h)	200	1 and 3,4 h	200
Result	No break	Breaks	No break
Observation	No cracks		No cracks

Overall conclusion

Citric acid passivation has proven to have same (or better) performances with respect to nitric acid passivation on the same steels.

Inputs for the LCA analysis

- Details of the passivation process conditions including all the sequences (pre-treatment, passivation and post-treatment) defined for each material
- Bath analysis (iron-build up) results
- Electricity consumption data (in kWh per m2 of treated material)
    - Passivated material quantity was normalised to 0,3m2 for all metals and treatments;
    - Industrial conditions (50ºC-60ºC) were considered both for nitric acid and citric acid passivation;

Thank you for your attention

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Quantis

LIFE CYCLE ASSESSMENT (LCA) OF NITRIC AND CITRIC ACID PASSIVATION PROCESS

FINAL LCA RESULTS FOR AISI 304L, AISI 316L, 13-8 PH, 15-5 PH, 17-4 PH, A286, AISI 321, AISI 440 AND CRONIDUR-30 STAINLESS STEELS

CONDUCTED BY ANNA KOUNINA
PRESENTED BY CHRISTOPHER ZIMDARS

clean space industrial days esa

25.10.2017

CONTEXT

1

Context and Scope of the LCA Study

- **Nitric acid** is currently the most widely used passivating solution. However, it has **multiple environmental, safety, and process disadvantages**
- **Citric acid** passivation has been recently proposed as a **green replacement** for stainless steels passivation processes due to several advantages:
  - Biodegradable and no hazardous waste
  - Does not create toxic fumes
  - Does not remove beneficial heavy metals from the surface

→ **Which of the two passivation processes has the better environmental performance?**

→ **LCA** is an appropriate tool to answer this question: It is an **internationally recognized approach** that evaluates the potential **environmental and human health impact** associated with products and services throughout their life

LCA METHOD & SYSTEM SCOPE

2

Life Cycle Design

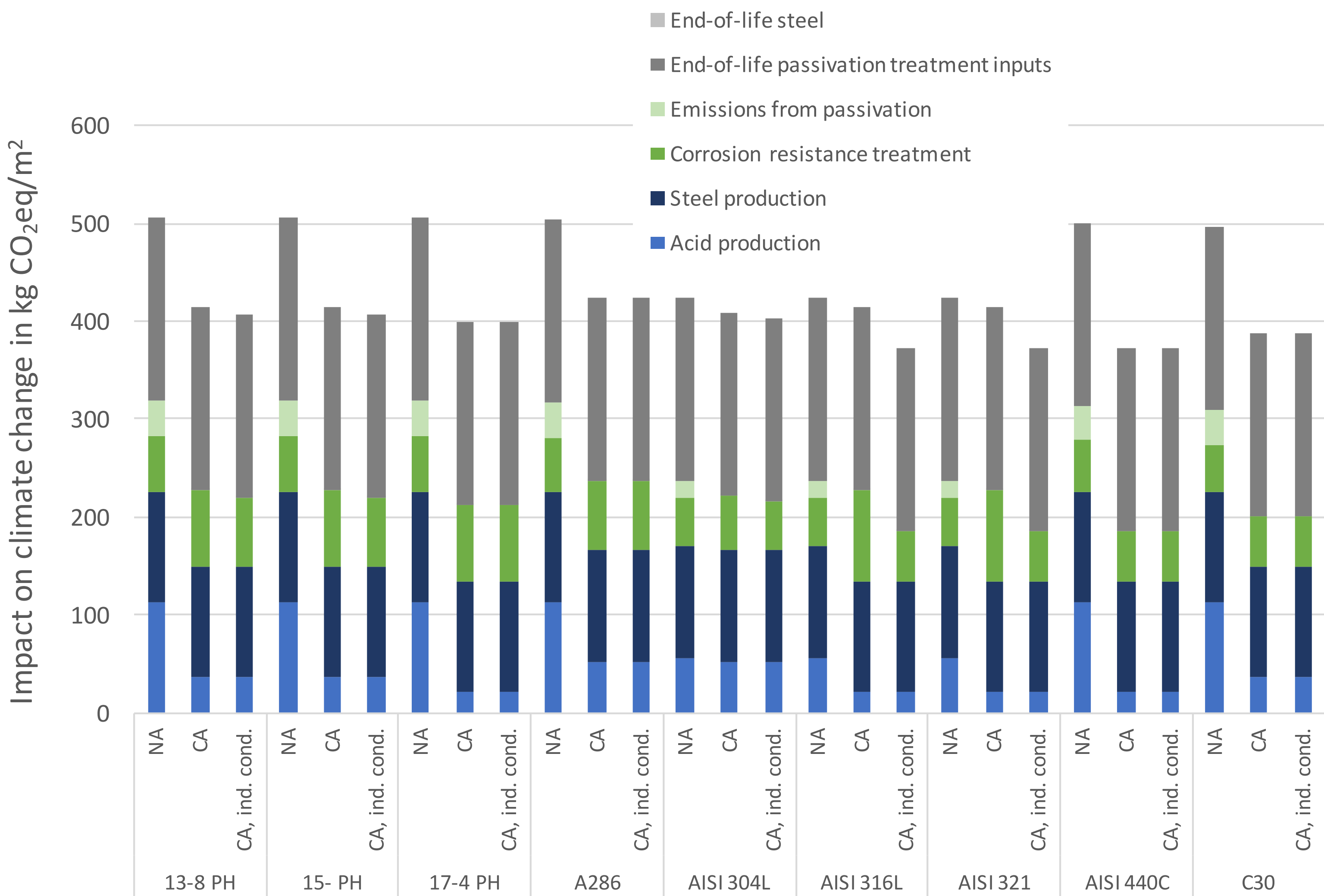
Life Cycle Stages of Stainless Steel

1. Acid production
2. Steel production
3. Corrosion resistance treatment process
4. Emissions from passivation
5. Use (negligible)
6. End-of-life of corrosion treatment inputs
7. End-of-life of steel

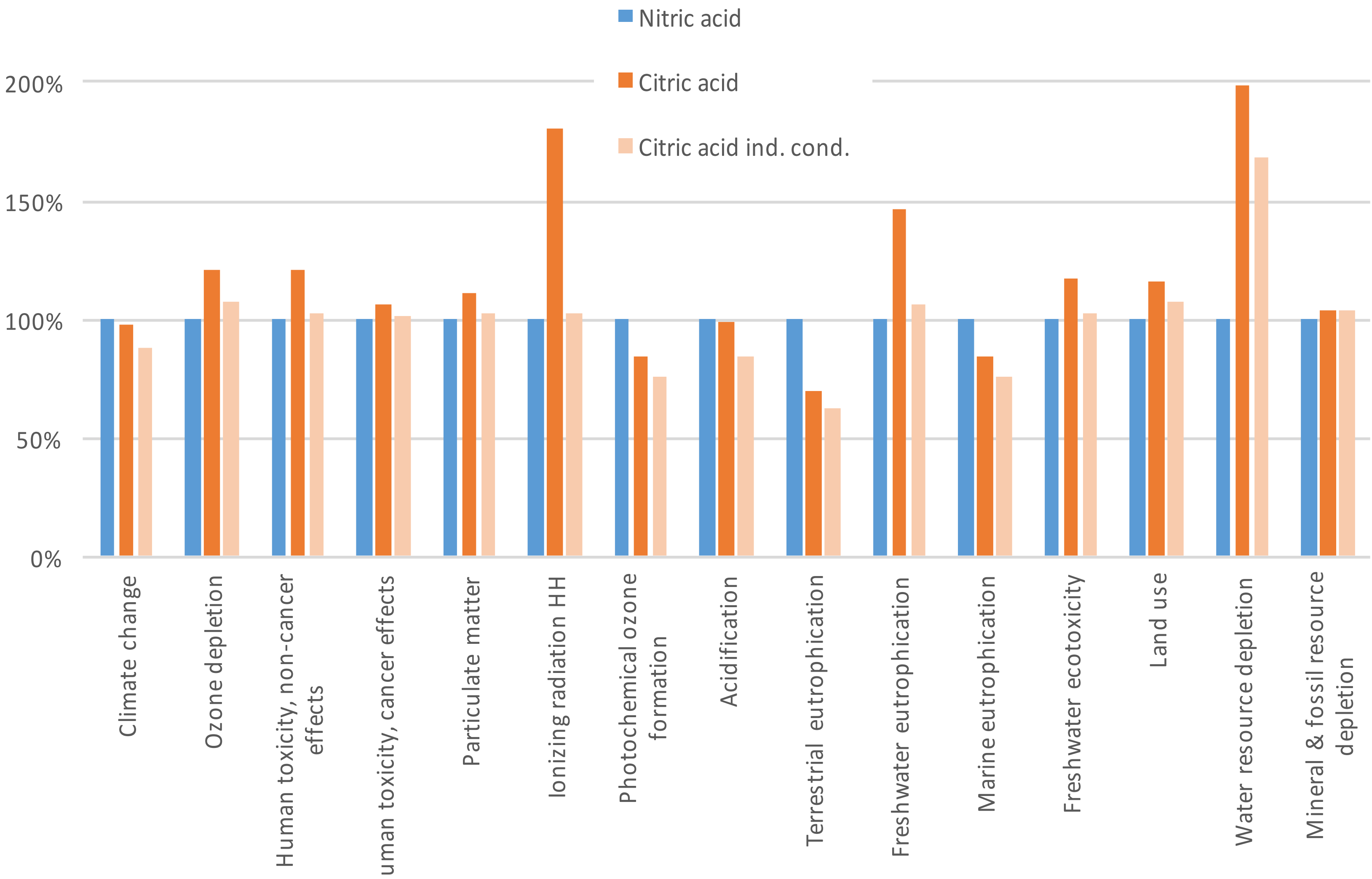
RESULTS

3

Impact on Climate Change of 9 steel types



Impact of AISI 321 steel on 15 ILCD categories



LIMITATIONS

4

Limitation of the conducted LCA study

- Passivation bath fumes
  - No data is available in the literature concerning the quantification of emissions associated with nitric acid passivation
  - Therefore, conservative assumptions and sensitivity analysis have been explored (from 0.1% to 10% of N emitted as HNO_3, NO, NO_2 and N_2O)
- Passivation bath end-of-life
  - No data is available on the nitric and citric acid end-of-life treatment, which is in fact a key environmental issue
  - Therefore, conservative assumptions have been explored (intensive pre-treatment or incineration for nitric acid)
- Extrapolation to the full industrial scale
  - Results provided in this study rely mainly on lab scale inventory data, industrial scale would be more adequate
  - Therefore, extrapolations based on expert guesses have been explored (reuse of bath to passivate larger steel surfaces)

CONCLUSIONS

5

Key Findings

- Nitric acid passivation: in general lower electricity use during passivation
- Citric acid passivation:
  - Reduced emissions from passivation
  - Potentially lighter treatment at end-of-life
- Impact of citric and nitric acid production varies depending on the considered impact category
- On full industrial scale, mainly acid bath fumes are expected to generate a difference in environmental impacts
  - The reuse of the passivation bath to treat a larger amount of steel surface would reduce acid inputs, electricity and end-of-life treatment

→ Nitric acid would be expected to have a larger environmental footprint (to verify using industrial scale data)

KEY MESSAGE

At full industrial scale, citric acid passivation is expected to be generally preferable to nitric acid passivation due to fumes from the acid bath, if the electricity consumption and acid quantities of both treatments are reduced due to the reuse of the passivation bath

These results need to be confirmed with industrial scale data

Thank you for your attention!

For any further Questions do not hesitate to contact us:

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