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**Distribution list:**

Person	Company
Advenit Makaya	ESTEC
Tommaso Ghidini	ESTEC
J. Marcos	TECNALIA
M. Brizuela	TECNALIA
E. Silveira	TECNALIA
Xabier Azpiroz	TECNALIA
Usua Izagirre	TECNALIA

**Modifications Control:**


Prepared by: Usua Izagirre, Elena Silveira, Marta Brizuela

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## 1 INTRODUCTION

### 1.1 SCOPE

This report describes the main findings of the project. 46238\_GREENACID: "Citric Acid as a Green Replacement for Steels passivation".

### 1.2 ACRONYMS

AD	Applicable Document
DoE	Design of Experiments
FT	Ferroxyl Test
LCA	Life Cycle Assessment
NA	Not Available
RD	Reference Document
SST	Salt Spray Test
WP	Work Package

### 1.3 APPLICABLE AND REFERENCE DOCUMENTS

#### 1.3.1 Applicable Documents

AD 1 Statement of Work "Citric Acid as a Green Replacement for Steels Passivation" TEC-QT/2014/95/TG.

AD 2 General Contract Conditions

AD 3 ECSS-Q-ST-70C, Materials, mechanical parts and processes.

AD 4 ECSS-Q-70-71A Rev. 1, Data for selection of space materials and processes.

AD 5 ECSS-Q-ST-70-36C, Material selection for controlling stress-corrosion cracking.

AD 6 ECSS-E-ST-10-03C, Testing.

AD 7 ECSS-Q-ST-70-45C, Standard methods for mechanical testing of metallic materials.

AD 8 ECSS-Q-ST-70-37C, Determination of the susceptibility of metals to stress-corrosion cracking.

#### 1.3.2 Reference Documents

RD1 ASTM380 Standard Practice for Cleaning, Descaling, and Passivation of Stainless Steel Parts, Equipment, and Systems

RD2 A967/A967M – 13 Standard Specification for Chemical Passivation Treatments for Stainless Steel Parts

RD3 AMS 2700 Passivation of Corrosion Resistant Steels.

RD4 Gaydos SP, Passivation of Aerospace Stainless Steel Parts with Citric Acid Solutions, The Boeing Company.

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RD5 Yasensky, D., Larson, C. and Reali, J., Citric Acid Passivation of Stainless Steel, Aircraft Airworthiness and Sustainment Conference, April 2011.

RD6 Passivation Treatment of Stainless Steel, Lena Wegrelius and Birgitta Sjöden, Outokumpu Stainless AB, ACOM, 4, 2004.

RD7 Alternative to Nitric Acid Passivation of Stainless Steel Alloys, Pattie L. Lewis, ITB, Inc./NASA Technology Evaluation for Environmental Risk Mitigation Principal Center (TEERM).

RD8 Alternative to Nitric Acid Passivation, DoD Corrosion Conference 2013. Pattie L. Lewis, ITB, Inc./NASA Technology Evaluation for Environmental Risk Mitigation Principal Center (TEERM).

RD9 Alternative to Nitric Acid Passivation, 2014 International Workshop on Environment and Alternative Energy, October 21-24 2014, Pattie L. Lewis, ITB, Inc./NASA Technology Evaluation for Environmental Risk Mitigation Principal Center (TEERM).

## 1.4 OBJECTIVES

The main objective of this Executive Summary Report is concisely summarized the main findings of the project.

## 2 SUMMARY OF MAIN ACTIVITIES

### 2.1 INTRODUCTION

Stainless steels are major manufacturing materials used in spacecraft and ground support structures on applications requiring corrosion resistance. Passivation of stainless steel has two main purposes: 1) it is necessary to remove free iron contamination left on the surface from machining and fabrication that can result in corrosion damage and 2) it forms 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. Citric acid passivation has been recently proposed as a green replacement for stainless steels passivation processes. It offers many advantages with regards to environmental impacts: it 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.

## 2.2 IDENTIFICATION OF TARGETED MATERIALS

In the following table is presented the summary of the alloys selected, welding process and material filler.

Material type	Alloy	EN	Selected welding process	Material filler
300 series	AISI 304L	1.4306	GMAW	308L
300 series	AISI 316L	1.4404	GMAW	316L
300 series	AISI 321	1.4541	GMAW	308L/347
400 martensitic	AISI 440C	1.4125	-	
400 martensitic	CRONIDUR 30	1.4108	-	-
P-H Martensitic	PH 17-4	UNS 17400	GTAW	ER 630
P-H Martensitic	PH 15-5	UNS 15500	GTAW	ER 630
P-H Martensitic	PH 13-8	UNS 13800	GMAW	308L
Other promising	A286	1.4980	-	

**Table 1:** Summary of the alloys selected, welding process and material filler.

## 2.3 NITRIC ACID VERIFICATION CAMPAIGN

The nitric acid passivation process verification was conducted on nine different stainless-steel materials by applying two best performing processes selected from relevant industry standards [RD1, RD2, RD3] and literature [RD4, RD5, RD6, RD7, RD8, RD9]. The effectiveness of passivation was verified by Salt Spray and Ferroxyl corrosion resistance tests as specified in the ASTM A967 and AMS 2700 specifications for stainless steel passivation, particularly with regard to the removal of free iron. The quantification of the passivation response for the salt spray test was done using image analysis software to get a percent (%) of the area that was corroded. The passivation response after the Ferroxyl test was quantified using a coloration-grade scale (that arbitrarily went from 0 to 8) to get a grade of the surface that was stained.

The selected treatment process for nitric acid passivation consisted of 1) a pre-treatment, which comprised an initial manual degreasing step with acetone, then a steel grit blasting sequence to introduce free iron and unpassivate the steel passive surfaces and then an immersion alkaline degreasing step; 2) the nitric acid passivation step and 3) a post-treatment, which comprised rinsing, drying and storage sequences.

**Table 2** summarises the operating values selected to nitric acid passivate the materials (in terms of HNO<sub>3</sub> concentration, processing time and temperature) and the followed selection logic.

**Table 3** summarises the passivation effectiveness responses after Salt Spray and Ferroxyl testing of specimens processed in the nitric acid passivation verification campaign.

**Table 4** shows the parameters that were fixed and selected for each material to treat the test specimens for the Characterisation Test Campaign in WP5. These results also served to provide a reference response for the citric acid optimisation process in WP4.

Austenitic grades (AISI 304L, AISI 316L, AISI 321)				
Treatment	[Nitric citric]	Temp. (°C)	Time (min)	Selection logic
1)	35% vol HNO <sub>3</sub> 67%wt	25°C	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 <sub>3</sub> 67%wt	55°C	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	[Nitric citric]	Temp. (°C)	Time (min)	Selection logic
1)	50% vol HNO <sub>3</sub> 67%wt	50°C	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 HNO <sub>3</sub> 67%wt + 2.5%wt sodium dichromate	50°C	30 min	Compliant with method Nitric 1 (ASTM A 967), with method I (ASTM A380) and with method Nitric 2 (AMS 2700C).

**Table 2** Selected operation values for nitric acid passivation of PH and martensitic materials.

Austenitic						
Material	Experiment #	[Nitric citric] *	Temp. (°C)	Time (min)	Salt Spray (%)*	Ferroxyl Grade (0 to 8)*
AISI 304L	Blank	Unpassivated	-	-	99,57%	8
	1	35% vol HNO <sub>3</sub> c.	25°C	45 min	7,95%	3,66
	2	25% vol HNO <sub>3</sub> c.	55°C	30 min	0,37%	1
AISI 316L	Blank	Unpassivated	-	-	98,58%	8
	1	35% vol HNO <sub>3</sub> c.	25°C	45 min	0,82%	2
	2	25% vol HNO <sub>3</sub> c.	55°C	30 min	0,82%	1
AISI 321	Blank	Unpassivated	-	-	98,97%	8
	1	35% vol HNO <sub>3</sub> c.	25°C	45 min	5,05%	3,83
	2	25% vol HNO <sub>3</sub> c.	55°C	30 min	0,82%	1
PH						
Material	Experiment #	[Nitric citric] *	Temp. (°C)	Time (min)	Salt Spray (%)*	Ferroxyl Grade (0 to 8)*
15-5 PH	Blank	Unpassivated	-	-	99,28%	8
	1	50% vol HNO <sub>3</sub> c.	50°C	30 min	39,46%	5,6
	2	25% vol HNO <sub>3</sub> c.+ 2.5%wt dichromate	50°C	30 min	98,15%	8
	3	50% vol HNO <sub>3</sub> c.	50°C	60 min	32,07%	5,5
	Repeat 3	50% vol HNO <sub>3</sub> c.	50°C	60 min	2,80%	-
4	50% vol HNO <sub>3</sub> c.	64°C	30 min	47,92%	5,25	
17-4 PH	Blank	Unpassivated	-	-	99,28%	8

	1	50% vol HNO <sub>3</sub> c.	50°C	30 min	19,92%	4,66
	2	25% vol HNO <sub>3</sub> c.+ 2.5%wt dichromate	50°C	30 min	96,99%	8
	3	50% vol HNO <sub>3</sub> c.	50°C	60 min	72,71%	5
	Repeat 3				1,03%	-
	4	50% vol HNO <sub>3</sub> c.	64°C	30 min	33,69%	4,75
	Repeat 4				3,13%	-
13-8 PH	Blank	Unpassivated	-	-	-	-
	3	50% vol HNO <sub>3</sub> c.	50°C	60 min	0,03%	-
A286	Blank	Unpassivated	-	-	19,5%	7,33
	1	50% vol HNO <sub>3</sub> c.	50°C	30 min	2,3%	4,16
	2	25% vol HNO <sub>3</sub> c.+ 2.5%wt dichromate	50°C	30 min	-	-
	3	50% vol HNO <sub>3</sub> c.	50°C	60 min	2,03%	2,5
	4	50% vol HNO <sub>3</sub> c.	64°C	30 min	1,20%	3,16
<b>Martensitic</b>						
Material	Experiment #	[Nitric citric] *	Temp. (°C)	Time (min)	Salt Spray (%)*	Ferroxyl Grade (0 to 8)*
AISI 440C	Blank	Unpassivated	-	-	41,83%	-
	1	50% vol HNO <sub>3</sub> c.	50°C	30 min	33,80%	-
	2	25% vol HNO <sub>3</sub> c. + 2.5%wt dichromate	50°C	30 min	73,47%	-
	3	50% vol HNO <sub>3</sub> c.	50°C	60 min	21,23%	-
	4	50% vol HNO <sub>3</sub> c.	64°C	30 min	20,37%	-
Cronidur® 30	Blank	Unpassivated	-	-	51,53%	-
	1	50% vol HNO <sub>3</sub> c.	50°C	30 min	8,63%	-
	2	25% vol HNO <sub>3</sub> c. + 2.5%wt dichromate	50°C	30 min	48,60%	-
	3	50% vol HNO <sub>3</sub> c.	50°C	60 min	16,60%	-
	4	50% vol HNO <sub>3</sub> c.	64°C	30 min	20,27%	-

**Table 3** Summary of Salt Spray and Feroxyl test responses of the test specimens processed in the nitric acid passivation verification campaign.

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

**Table 4** Selected passivation conditions in the nitric acid passivation verification campaign.

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## 2.4 CITRIC ACID PASSIVATION OPTIMISATION CAMPAIGN

The citric acid passivation process optimisation was conducted on nine different stainless-steel materials using Design of Experiments (DoE) instrument and was focused on evaluating the influence of three main parameters (i.e. 1- concentration of citric acid in the bath, 2- process temperature and 3- processing time) in the effectiveness of passivation for each of the nine materials. The process parameters selected to be studied were varied at two different levels. The lower and upper limit values defined for each family of materials were selected in consistency with relevant industry standards [RD1, RD2, RD3] and literature [RD4, RD5, RD6, RD7, RD8, RD9]. In particular, the citric acid concentration limits selected for all materials were 4wt% and 10wt%, to make them consistent with the limits allowed by the ASTM A967 and AMS2700 standards for citric acid passivation. Higher concentration ranges were analysed in other studies [RD4, RD5] but were not selected in this work since the mentioned studies concluded that concentration had small effect. Regarding temperature, the high limit value selected was 85°C, in consistence with the upper limits defined by the NASA in their latest studies [RD7, RD8, RD9]. For processing time, the high limit value selected for austenitic materials was 150 min, in consistency with the consulted literature [RD4 to RD9] and taking into account, that, according to these studies, corrosion protection improved with time. For PH and martensitic grades, the maximum time was reduced to 90 min since the optimum processing times obtained by NASA [RD7 to RD9] were 60 min or lower for the PH and 400 series alloys. Yasensky [RD5] also concluded for 17-4 PH and AISI 440C that beyond 30 min processing time had little effect.

The selected treatment process for citric acid passivation was the same as for nitric acid passivation and consisted of 1) a pre-treatment, which comprised an initial manual degreasing step with acetone, then a steel grit blasting sequence to introduce free iron and unpassivate the steel passive surfaces and then an immersion alkaline degreasing step; 2) the nitric acid passivation step and 3) a post-treatment, which comprised rinsing, drying and storage sequences.

For each material and treatment, two responses – i.e. response in Salt Spray test and in Ferroxy test were measured and analysed statistically to study the influence of the selected factors and to optimise the quality of the passivation. Nitric acid passivated and “unpassivated” specimens were tested as reference processes. The rest of the process parameters were fixed and remained constant within a minimum range. Experimental Design software STATGRAPHICS Centurion XVI version 16.2.04 was used for the experimental definition and analysis of results.

The optimisation consisted on looking for the combination of parameters that gave the minimum percent of corroded area in salt spray test, within the experimental conditions selected in this work. The final optimum parameters were chosen secondly considering the optimisation of the mathematical model obtained for the Ferroxy Test. Finally, if the influence of a given factor resulted insignificant in the corrosion response, the minimum values were considered for process optimisation.

**Table 5** summarises the lower and upper limit values for citric acid concentration, process temperature and time defined for each family of materials.

**Table 6** and **Table 7** summarise the equations or models given by the DoE analysis for Salt Spray response and Ferroxy response, respectively. The tables also show the values



predicted by the models for Salt Spray and FerroxyI response at the selected optimum conditions in comparison with the actual values, i.e. Salt Spray and FerroxyI responses obtained experimentally working at the selected optimum conditions.

**Table 8** shows the parameters that were fixed and selected as optimum for each material to treat the test specimens for the Characterisation Test Campaign in WP5.

Austenitic grades (AISI 304L, AISI 316L, AISI 321)		
Factors	Lower limit	Upper limit
Citric acid concentration	4 wt %	10 wt %
Temperature	25°C	85°C
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	25°C	85°C
Treatment time	15 min	90 min

**Table 5** Upper and lower limits (levels) defined for each factor (parameter) considered in the statistical study for the different grades.

Material	DoE Model (SST Corroded area %)	Optimised process parameters			Predicted value (SST Corroded area %)	Actual value (SST Corroded area %)
		Citric acid (wt%)	Temp (°C)	Time (min)		
AISI 304L	Does not fit to a statistical model. All experimental runs achieved the target 0% corroded area.	4%	85°C	15´	0%	0%
AISI 316L	$SST_{\text{corroded area}} (\%) = 0,419 - 0,005 \cdot \text{Bath Temperature} - 0,003 \cdot \text{time} + 0,00003 \cdot (\text{Bath temperature} \times \text{time})$	4%	85°C	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%	85°C	150´	0%	0%
15-5 PH	$SST_{\text{corroded area}} (\%) = 176,79 - 3,47 \cdot \text{Citric acid concentration} - 3,37 \cdot \text{Bath temperature} - 0,32 \cdot \text{time} + 0,02 \cdot (\text{Bath temperature})^2$	7%	85°C	90´	1.78±13.78%	0.33%
17-4 PH	$SST_{\text{corroded area}} (\%) = 38,10 - 0,005 \cdot (\text{Bath temperature} \times \text{time})$	4%	85°C	90´	1.22±12.70%	0.66%
13-8 PH	-	7%	85°C	90´	-	0.03%
AISI A286	$SST_{\text{corroded area}} (\%) = -0,24 + 0,25 \cdot \text{Bath temperature} - 0,016 \cdot (\text{Citric Acid Concentration} \times \text{Bath temperature}) - 0,001 \cdot (\text{Bath temperature} \times \text{time})$	10%	85°C	90´	-3.55±4.23%	0.33%

AISI 440C	$SST_{\text{corroded area}} (\%) = 114,89 - \text{Bath Temperature} - 1,91 \cdot \text{time} + 0,018 \cdot (\text{time})^2$	4%	85°C	60'	- 18.53±4.53%	6.00%
C®30	$SST_{\text{corroded area}} (\%) = 13,16 - 0,38 \cdot \text{time} - 0,024 \cdot (\text{Citric Acid Concentration} \times \text{Bath Temperature}) + 0,12 \cdot (\text{Citric Acid Concentration})^2 + 0,004 \cdot (\text{time})^2$	7%	85°C	60'	-4.16±2.4%	0.77%

**Table 6** Summary of DoE models for salt spray response, and predicted and actual values at the optimised conditions.

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 (°C)	Time (min)		
AISI 304L	$\text{Ferroxyl grade} = 2,701 + 0,330 \cdot \text{Citric Acid Concentration} - 0,023 \cdot \text{time} - 0,007 \cdot (\text{Citric Acid Concentration} \times \text{Bath temperature}) + 0,0003 \cdot (\text{Bath temperature} \times \text{time})$	4%	85°C	15'	0.45±0.82	1.83
AISI 316L	$\text{Ferroxyl grade} = 6,127 - 0,062 \cdot \text{Bath Temperature} - 0,032 \cdot \text{time} + 0,0003 \cdot (\text{Bath temperature} \times \text{time})$	4%	85°C	150'	0.11±0.78	0.3
AISI 321	$\text{Ferroxyl grade} = 4,785 - 0,035 \cdot \text{Bath Temperature} - 0,01 \cdot \text{time}$	4%	85°C	150'	0.22±0.65	0.83
15-5 PH	$\text{Ferroxyl Grade} = 6,30 - 0,001 \cdot (\text{Bath temperature} \times \text{time}) + 0,0004 \cdot (\text{time})^2$	7%	85°C	90'	0.86±1.41	3.17
17-4 PH	$\text{Ferroxyl Grade} = 10,68 - 0,008 \cdot \text{Bath temperature} - 0,0004 \cdot (\text{Bath temperature} \times \text{time})$	4%	85°C	90'	1.03 ± 1.28	1.66
13-8 PH	-	7%	85°C	90'	-	-
AISI A286	$\text{Ferroxyl grade} = 11,40 - 0,70 \cdot \text{Citric Acid Conc.} - 0,02 \cdot \text{Bath temperature} - 0,07 \cdot \text{time} + 0,006 \cdot (\text{Citric Acid Concentration} \times \text{time})$	10%	85°C	90'	1.91±0.71	1.83
AISI 440C	-	4%	85°C	60'	-	-
C®30	-	7%	85°C	60'	-	-

**Table 7** Summary of DoE models for Ferroxy response, and predicted and actual values at the optimised conditions.

Material	[Citric citric] (wt%)	Temp. (°C)	Time (min)	Salt Spray (%)*	Ferroxyl Grade (0 to 8)*
AISI 304L	10 wt.% citric acid	85°C	15 min	0%	1.83
AISI 316L	4 wt.% citric acid	85°C	150 min	0%	0.3
AISI 321	4 wt.% citric acid	85°C	150 min	0%	0.83
15-5 PH	7 wt.% citric acid	85°C	90 min	0.33%	3.17
17-4 PH	4 wt.% citric acid	85°C	90 min	0.66%	1.66
13-8 PH	7 wt.% citric acid	85°C	90 min	0.03%	-
AISI A286	10 wt.% citric acid	85°C	90 min	0.33%	1.83

AISI 440C	4 wt% citric acid	85°C	60 min	6.00%	-
C@30	7 wt% citric acid	85°C	60 min	0.77%	-

**Table 8** Selected passivation conditions in the citric acid passivation optimisation campaign.

## 2.5 LIFE CYCLE ASSESSMENT

In order to compare the environmental performance of both passivation processes, the environmental impact of both nitric and citric acid passivation through Life Cycle Assessment (LCA) was assessed following the main guidelines of the ILCD Handbook and the ISO norms 14040-14044. The passivation of nine stainless steels has been analysed, and experimental data have been used as the inventory in this LCA.

**Figure 1** shows the climate change impact of all tested steels for nitric and citric acid passivation, with the differentiation between normalized laboratory scale electricity use and industrially relevant electricity use for citric acid passivation.

Impact results are driven by the following main life-cycle components:

- **Acid production:** Considering the inventory and impact per kg acid, nitric acid production has a higher contribution to climate change than citric acid production, however this trend is not valid for all impact categories.
- **Steel production and end-of-life:** A 25 kg chromium steel production is considered for both passivation processes and has a substantial contribution to most impact categories. However, it has the same impact for both passivation processes.
- **Corrosion resistance treatment:** The electricity use to heat the passivation bath is key to determine whether nitric or citric acid passivation will be more impactful, and this depends on the analysed steel (for most of them, electricity consumption for nitric acid passivation is lower than for citric acid passivation, even when the latter is extrapolated to industrially relevant passivation temperatures).
- **Emissions from passivation:** The nitric acid bath emits nitric acid mist droplets (HNO<sub>3</sub>), NO<sub>x</sub> and N<sub>2</sub>O that contribute to climate change, photochemical ozone formation, acidification as well as terrestrial and marine eutrophication. This **makes nitric acid passivation more impactful than citric acid passivation** for all these mentioned impact categories. Regarding toxic impact on human health, HNO<sub>3</sub> has a proved effect on non-cancer diseases, and is suspected to have a carcinogenic effect that could not be analysed in this study due to lack of data. We considered only CO<sub>2</sub> emissions from the citric acid bath.
- **End-of-life of passivation inputs:** We assume that the acetone, alkaline cleaner and passivation bath are treated as hazardous waste and incinerated for both nitric acid and citric acid baths. This is a conservative assumption and a sensitivity analysis on intensive wastewater treatment shows a lower contribution on climate change than for incineration. In case the citric acid bath is treated as wastewater while the nitric acid bath is incinerated, this would provide a lower impact for the citric acid passivation end-of-life.

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**Figure 1** shows that nitric acid passivation is more impactful on climate change than citric acid passivation for all steels, especially due to the dinitrogen monoxide (powerful greenhouse gas) released during the nitric acid production. **Figure 2** shows the same results, without the contribution of steel production.

**Figure 3** shows results for AISI 321 steel, where citric acid passivation extrapolated at industrial conditions (at industrially relevant passivation temperatures) is close to (within 10% difference) or less impactful than nitric acid passivation for most impact categories except water resource depletion. The much higher impact of citric acid passivation on water resource depletion is due to higher water consumption during the citric acid production process compared to nitric acid production. **Figure 4** shows the same results, without the contribution of steel production, where the results show approximately the same trend except for mineral and fossil resource depletion. This latter impact indicator is totally dominated by steel production. However, when steel production is not considered, the higher impact of citric acid production in comparison to nitric acid production on mineral and fossil resource depletion is highlighted.

A key parameter that makes **nitric acid** environmentally preferable to citric acid is the **lower electricity use** during passivation (electricity is however likely to be significantly reduced for both citric and nitric acid at full industrial scale).

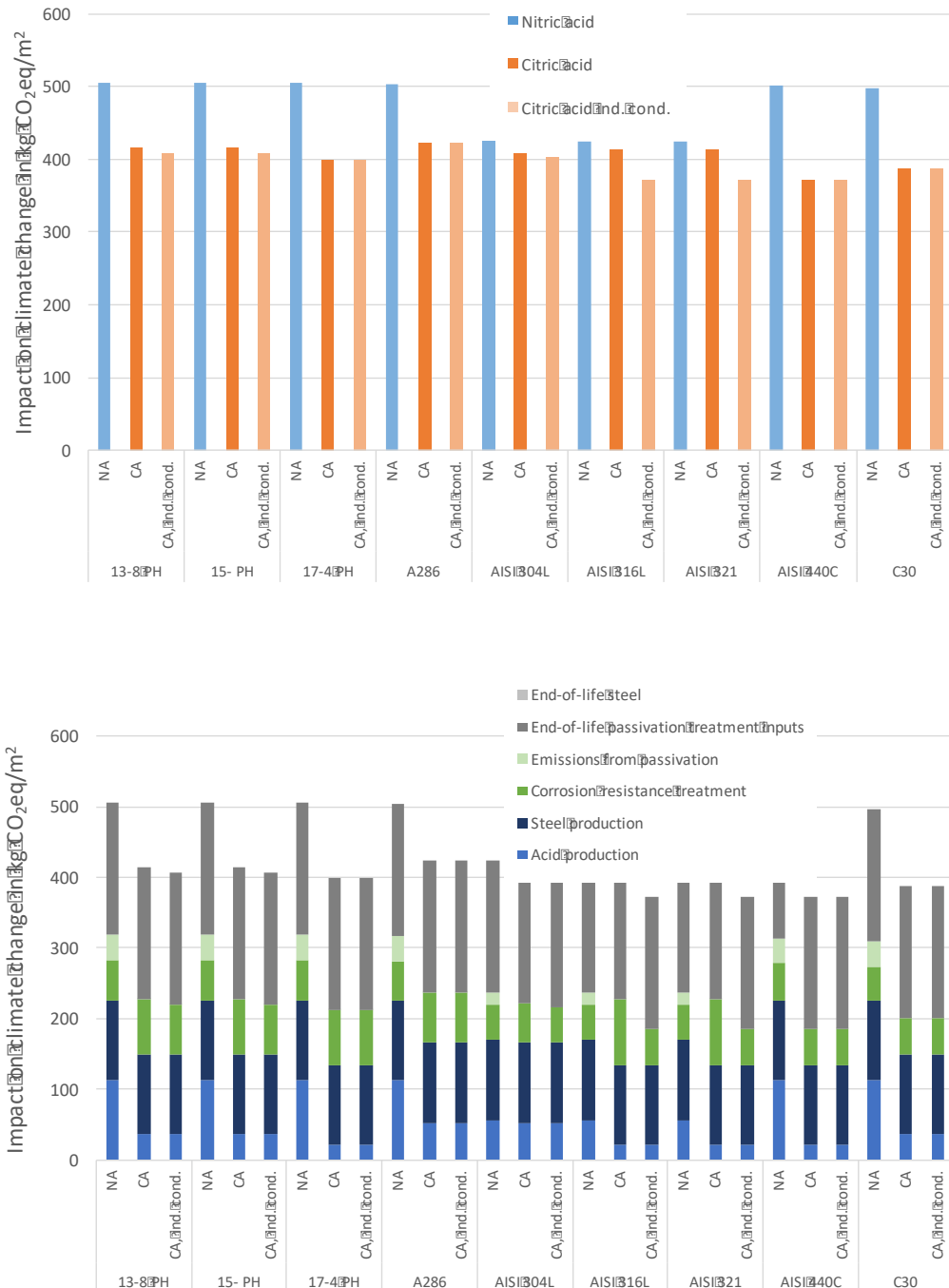
Key parameters that make **citric acid** environmentally preferable are 1. the **reduced emissions** from passivation (the human health cancer effect and ecotoxicity effects of nitric acid are not included in this study because of lack of (eco)toxicity data, this could thus emphasize the lower toxic effect of citric acid) and 2. the **potentially lighter treatment** at end-of-life (citric acid could be potentially treated as wastewater instead of being incinerated, but this needs to be confirmed by an external expertise).

The comparison of the environmental impact of **citric** and **nitric acid production** depends on impact categories (citric acid production in the required quantities can be more or less impactful than nitric acid production depending on the considered impact category).

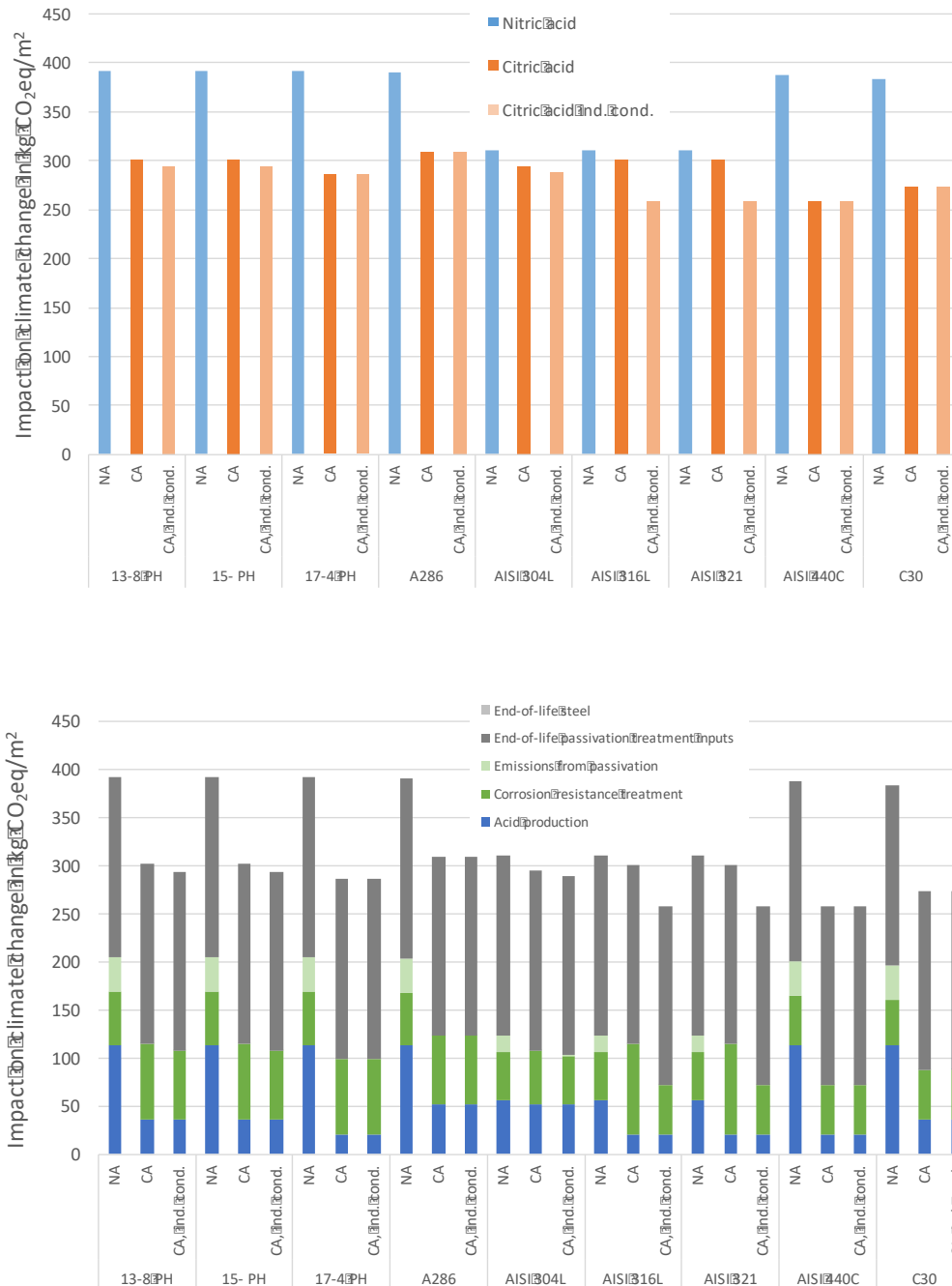
When extrapolating to the full industrial scale, key differences between the two passivation methods can become negligible if the passivation bath is reused several times to passivate a larger amount of steel surfaces, reducing the acid and electricity inputs as well as the end-of-life treatment requirement. In the latter case, only acid bath fumes would drive differences in the environmental impact between the two passivation methods, thus nitric acid would have a larger environmental footprint than citric acid passivation.

As a key conclusion, we can say that **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** with the reuse of the passivation bath to passivate larger surfaces of steel (thus lower electricity requirements for heating and lower amount of acid requirements per unit stainless steel surface).

It is recommended to perform a life cycle assessment of a full industrial scale passivation to confirm these conclusions.



**Figure 1** Climate change impact of nitric acid and citric acid passivation for all analysed steels, with normalized laboratory scale electricity use and with industrially relevant electricity use, global and detailed figure.



**Figure 2** Climate change impact of nitric acid and citric acid passivation for all analysed steels, with normalized laboratory scale electricity use and with industrially relevant electricity use, global and detailed figure, without steel production contribution.

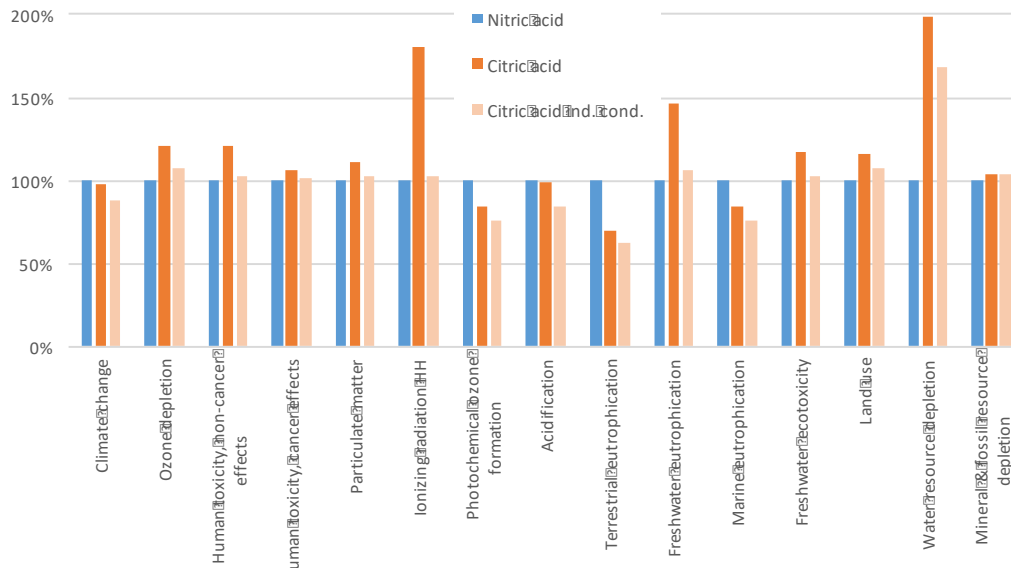


Figure 3 Overall results of nitric acid, citric acid with lab scale electricity use and with industrially relevant electricity use for bath heating at 60° for all ILCD impact indicators.

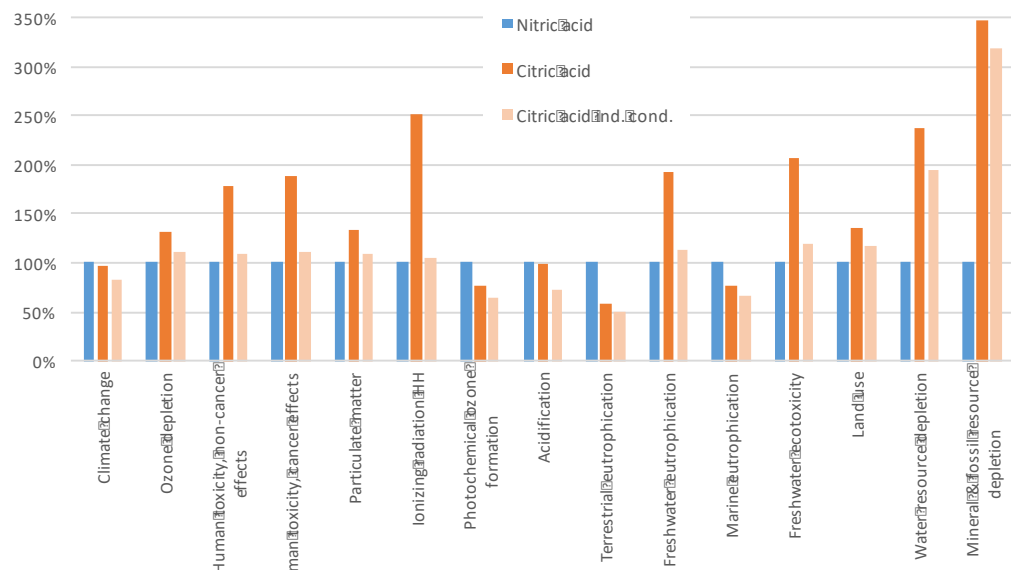


Figure 4 Overall results of nitric acid, citric acid with lab scale electricity use and with industrially relevant electricity use for bath heating at 60° for all ILCD impact indicators, without steel production contribution.

## 2.6 CHARACTERISATION TEST CAMPAIGN

Nitric acid and citric acid passivated materials were subjected to an extensive characterisation campaign in WP5. The test campaign was conducted onto nine different stainless-steel

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materials using test coupons both in pristine and in welded conditions. For each material, the applied nitric acid and citric acid passivation parameters corresponded to the best performing process conditions previously identified during the verification and optimisation campaigns in WP3 and WP4. The objective of the test campaign was to compare the performance of the stainless-steel materials passivated with nitric and citric acid both in pristine and in welded conditions.

The test campaign included characterisation tests such as chemical composition determination by optical emission spectroscopy, surface chemical composition determination by XPS, hydrogen content measurements, hardness and microhardness determination and microstructural characterisation. Mechanical properties after passivation were determined by tensile tests, axial fatigue tests and fatigue crack propagation tests. Corrosion resistance properties after passivation were examined by salt spray corrosion testing, electrochemical tests (open circuit potential and potentiodynamic measurements), stress corrosion cracking (SCC) tests and hydrogen embrittlement tests.

The results showed that, in general, the mechanical properties of nitric acid and citric acid passivated samples were comparable for all tested materials and no significant differences were found in terms of hydrogen content, hardness, microhardness, microstructure, tensile testing and fatigue crack propagation between nitric acid and citric acid passivated specimens. No relevant differences were either found between passivated and unpassivated specimens. This means that none of the passivation processes tested (neither nitric or citric) resulted detrimental for the mechanical properties of the tested materials. In other words, the passivation process did not show influence on the mechanical properties of the bulk materials. This is particularly relevant for the citric acid passivated materials, where more severe process conditions were used comparing with nitric acid passivation, i.e. higher temperatures and longer processing times.

Related to the above, no relevant differences were found in hydrogen embrittlement performance considering both types of passivation and all austenitic and PH materials passed the embrittlement test. Regarding martensitic materials, which are the most sensitive ones to hydrogen embrittlement among the tested materials due to their high strength, the citric acid passivated specimens passed the test with the 440 C material while the nitric acid passivated ones failed. This is an interesting finding considering that the citric acid passivation was done using higher temperatures and longer times than nitric acid passivation. Anyway, further extended testing should be done to confirm this result.

Some differences were found in the fatigue performance of austenitic and PH materials comparing nitric acid and citric acid passivation. In the case of austenitic materials, the fatigue limit was lower for 316L passivated with citric acid vs. nitric acid when tested at a stress ratio of R1 while the fatigue limit was significantly lower for 321 passivated with nitric acid vs. citric at the same R ratio. For PH materials, the fatigue limit of both 17-4 PH and 15-5 PH materials was higher for specimens passivated with citric acid vs. nitric acid when tested at a stress ratio of R0.1. This difference was not evident at a stress ratio of R1. Anyway, in all studied cases it was difficult to determine if the observed differences were attributable to the passivation process or to the dispersion of the test itself, also considering that the specimens subjected to fatigue testing were the welded ones, which can induce more dispersion.

Unlike the mechanical properties, the corrosion resistance properties were in general significantly influenced by the passivation process and relevant differences were also found depending on the type of passivation used.



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Regarding salt spray testing, austenitic materials performed well after 168h of SST both for unpassivated and passivated specimens. The good results for the unpassivated specimens can be attributed to the passive layer that is naturally formed on the surface of austenitic materials in aerated environments and the lack of any free iron or other contaminants in the specimens subjected to testing.

Interestingly, SST results showed that the corrosion resistance performance of 17-4 PH, 15-5 PH, 13-8 PH, 440-C and C-30 was significantly improved for citric acid passivated specimens in comparison to nitric acid passivated and unpassivated specimens. This was especially relevant for C-30, 13-8PH and 15-5PH materials, followed by 17-4PH and 440-C, in the latter case the improvement not being so relevant. On the contrary, citric acid passivated A286 test specimens showed a poor result in SST, considerably worse than for nitric acid passivated and unpassivated specimens. Further testing is suggested to be done to elucidate the reasons of this isolated behaviour.

The SST results were mostly supported by the results obtained in the electrochemical measurements. In the case of austenitic materials, none of the passivation types tested induced a significant improvement with respect to the unpassivated condition. In the case of PH materials, the passivated specimens behaved better than the unpassivated ones, but no significant differences were observed between both types of passivation, unlike in SST where corrosion resistance improvement with citric acid was noticeable compared to the nitric acid passivation and the unpassivated condition. In the case of martensitic materials, interestingly, citric acid passivation showed better performance than nitric acid passivation and the unpassivated conditions, supporting the trends observed in SST. The electrochemical tests also confirmed the poor corrosion resistance result of the A286 material.

Regarding SCC that was conducted according to the ECSS-Q-ST-70-37C standard on the austenitic materials, the results permitted to classify these materials as “highly resistance to stress corrosion”, as was expected.