December, 2014

ROYAL INSTITUTE
OF TECHNOLOGY

Surface changes and metal release in the presence of citric acid for food applications Stainless steel grades 201, 304, 204, 2101, 316L, 430, and EN1.4003

Final report, December 2014

Neda Mazinanian, Inger Odnevall Wallinder, and Yolanda Hedberg

nedam@kth.se; ingero@kth.se; yolanda@kth.se
KTH Royal Institute of Technology,
Division of Surface and Corrosion Science, Sweden

Commissioned by Team Stainless

ROYAL INSTITUTE OF TECHNOLOGY

Metal release from stainless steel into citric acid and tap water solutions of relevance for food applications with a surface perspective

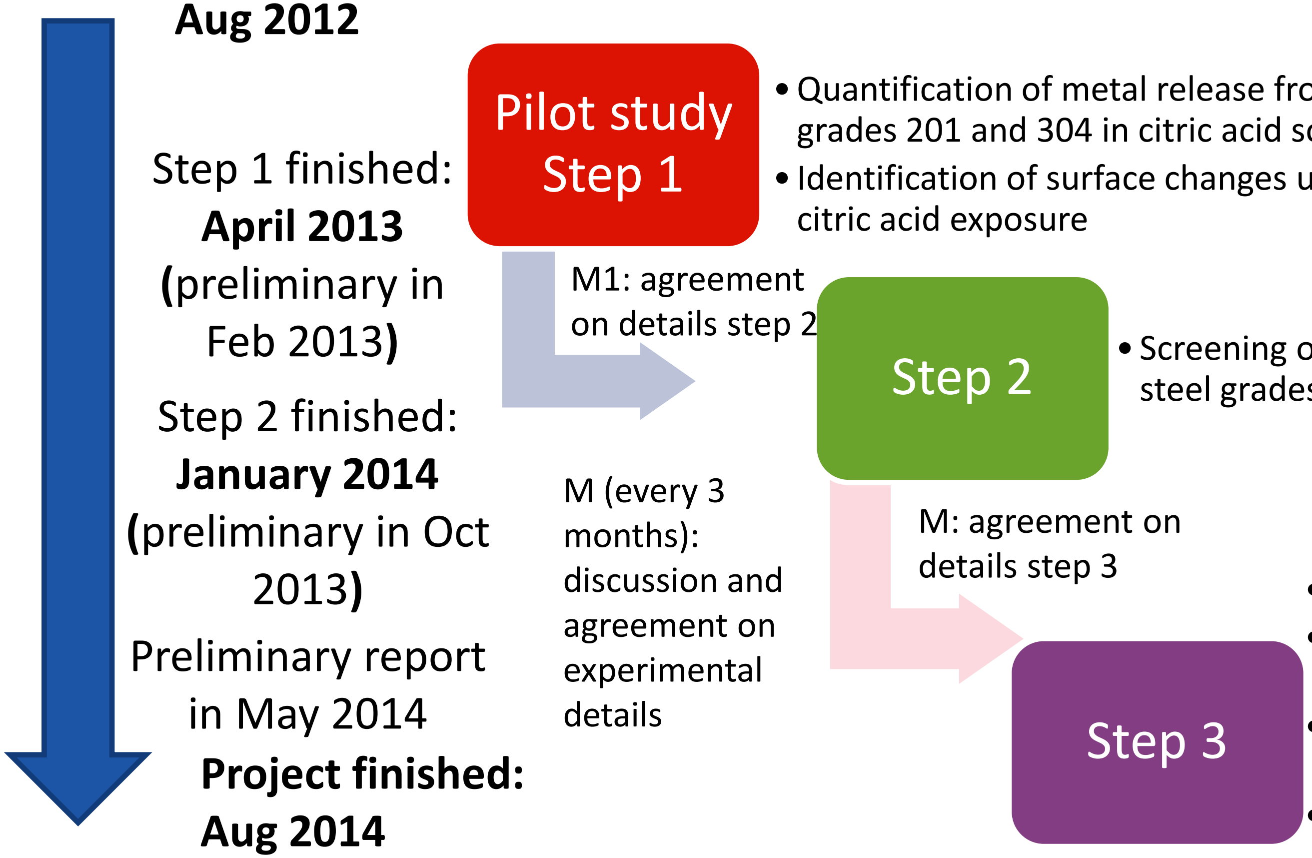
KTH – Team Stainless project, Aug 2012 – Aug 2014

Background: Implementation of the new CoE protocol, using citric acid instead of acetic acid (Italian decree) as test medium.

Important ***research questions*** answered:

1. ***Differences in released metal quantities*** from stainless steel grades when using the new CoE protocol, compared to the Italian decree?
2. How is the ***surface of stainless steels changed*** upon exposure in citric acid? Is there any possibility of formation of Cr(VI) due to the oxidizing potential of any manganese oxides in the surface oxide of manganese-containing stainless steels?
3. How will ***different stainless steel grades of diverse surface finish*** behave following exposure according to the CoE protocol? Which grades will pass and which grades will fail the requirements, and at what specific conditions (loading, temperature, repeated exposures, etc.)?
4. Influence of the ***pH and citric acid concentration*** of the solution, respectively, on the released amount of metals from stainless steel?
5. *How is the influence of* ***repeated exposure*** *in citric acid and* ***surface abrasion*** *on the metal release from some stainless steel grades?*

Time line



START:
Aug 2012

Step 1 finished:
April 2013
(preliminary in
Feb 2013**)**

Step 2 finished:
January 2014
(preliminary in Oct
2013**)**

Preliminary report
in May 2014

Project finished:
Aug 2014

Final draft report:
latest December
2014

Pilot study
Step 1

- Quantification of metal release from grades 201 and 304 in citric acid solutions
- Identification of surface changes upon citric acid exposure

M1: agreement on details step 2

Step 2

- Screening of different stainless steel grades

M (every 3 months): discussion and agreement on experimental details

M: agreement on details step 3

Step 3

- Effect of repeated exposure
- Effect of pH and citric acid concentration
- Investigation of different surface finishes for 316 and 304
- Effect of loading (surface area to solution volume ratio) for as-received 304 (2B)

M – meeting (email, telephone conference, meeting) between KTH and working group (sponsor(s))

Investigated grades

Investigated grades of stainless steels (based on supplier information)

Name (in this report)	UNS (ASTM A 240)	EN	Surface finish	Cr wt%	Mn wt%	Ni wt%	Mo wt%	Cu wt%	N wt%	C wt%	S wt%
EN1.4003	S40977	1.4003	2B	11	1	< 1	-	-	-	-	-
430	S43000	1.4016	2B	16	0.3	0.1	0.02	0.04	0.03	0.03	0.002
204	S20431 (+Cu)	1.4597 (+Cu)	2B	16	9.1	1.1	0.2	1.6	0.19	0.1	0.004
201	S20100	1.4372	2D	16.9	5.8	3.6	0.2	0.4	0.15	0.11	0.002
316L	S31603	1.4404	2B	17	1.3	10.2	2.0	0.5	0.05	0.02	-
316L	S31603	1.4404	Sc.-Br. (2J)	using a Scotch-Brite brush							
316L	S31603	1.4404	No. 4 (2G)	polishing with a 220 grit grinding belt							
304	S30400	1.4301	2B	17.9	1.2	9.0	0.4	0.4	0.04	0.04	0.003
304	S30400	1.4301	Sc.-Br. (2J)	using a Scotch-Brite brush							
304	S30400	1.4301	No. 4 (2G)	polishing with a 320 grit grinding belt							
LDX 2101	S32101	1.4162	2B	21.4	4.8	1.6	0.3	0.3	0.22	0.02	0.001

Surface preparation of test coupons

As-received: Edges ground (abraded) by 1200 grit SiC, coupon areas not abraded, cleaned ultrasonically in ethanol and acetone for 5 min, respectively, dried with cold nitrogen gas, and aged for 24 ± 1 h in a desiccator (at room temperature).

Abraded: Edges + coupon surfaces abraded (1200 grit SiC), otherwise identical preparation as for as-received coupons.

Synthetic fluids + exposure conditions

Exposures after
2, 4, 8, 26 , 240 h
(70°C (first 2 h) / 40°C), CoE protocol

All citric acid test solutions were buffers with pH changes during exposure of less than 0.19

Temperature, surface preparation, solution, loading, and exposure duration differ, as described for each result.

CoE protocol →

<u>Citric acid, pH 2.4</u> (CA 2.4) 5 g/L citric acid

<u>Citric acid, pH 3.1</u> (CA 3.1)
5 g/L citric acid + 850 µg/L (NaOH 50%)

<u>Citric acid, pH 4.8</u> (CA 4.8)
5 g/L citric acid + 2980 µg/L (NaOH 50%)

<u>Citric acid, pH 6.4</u> (CA 6.4)
5 g/L citric acid + 4280 µg/L (NaOH 50%)

<u>Citric acid, pH 11</u> (CA 11)
5 g/L citric acid + 4550 µg/L (NaOH 50%)

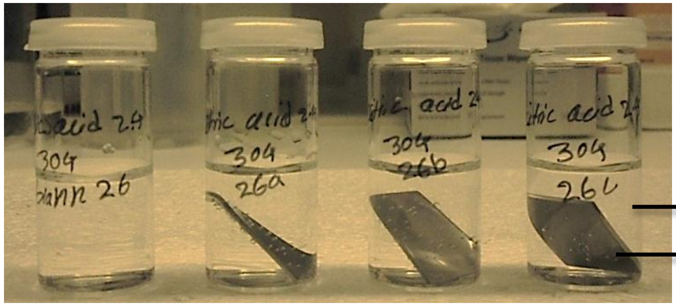
Investigation of the effect of pH and citric acid concentration

<u>Citric acid, pH 4.5</u> (CA 4.5)
20.8 g/L citric acid, 6 g/L NaOH

← ***Same CA amount and pH as in artificial lysosomal fluid (previous studies)***

<u>Artificial tap water, pH 7.5</u> (TW)
0.12 g/L $NaHCO_3$, 0.07 g/L $MgSO_4{*}7H_2O$, 0.12 g/L $CaCl_2{*}2H_2O$

← ***CoE protocol***

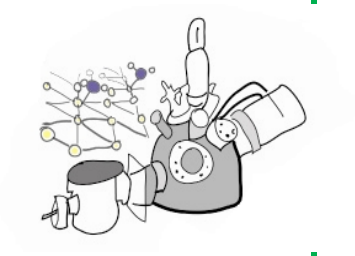


→ 6 mL test solutions

→ Samples - total surface area: approx. 6 cm²

→ Loading of 1 cm²/mL

Experimental strategy



Surface characterization (prior and after exposure, selected samples):

- Scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS)
- Confocal Raman microscopy (CRM)
- X-ray photoelectron spectroscopy (XPS)
- Electron Backscattered Diffraction (EBSD)

Electrochemical measurements:
Open circuit potential (OCP) time- and temperature-dependence

Solution analysis:
Atomic absorption spectroscopy – graphite furnace (GF-AAS):

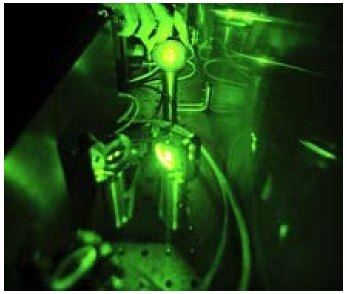
Fe, Cr, Ni, Mn, Mo (only for grade 316)

Speciation analysis (grades 201 and 304):
Stripping voltammetry:

Cr(III), Cr(VI)

Raman spectroscopy (201 and 2101):

After exposure, especially to citric acid pH 2.4:



- *different iron oxides*
- *possibly chromium(III)oxides*
- *no evidence for chromates*
- *different manganese oxides possible*

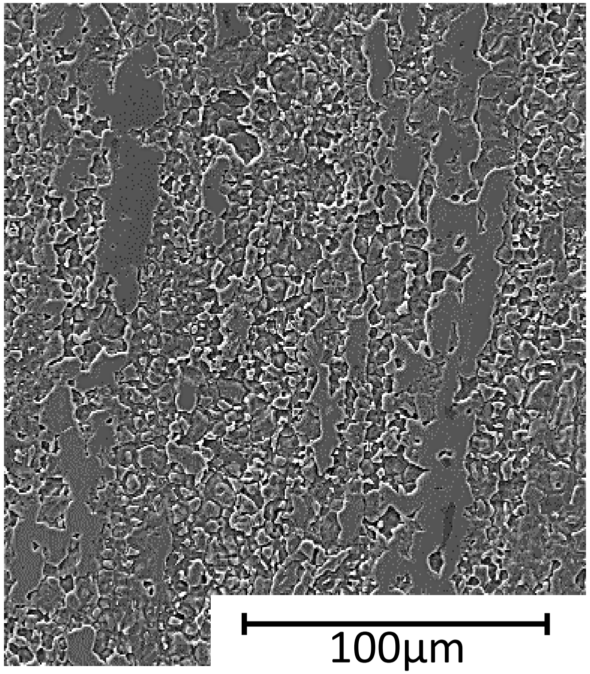
EDS results (201, 304, and 2101)

in general agreement with bulk information provided by the supplier.

Homogenous elemental distribution for 304.

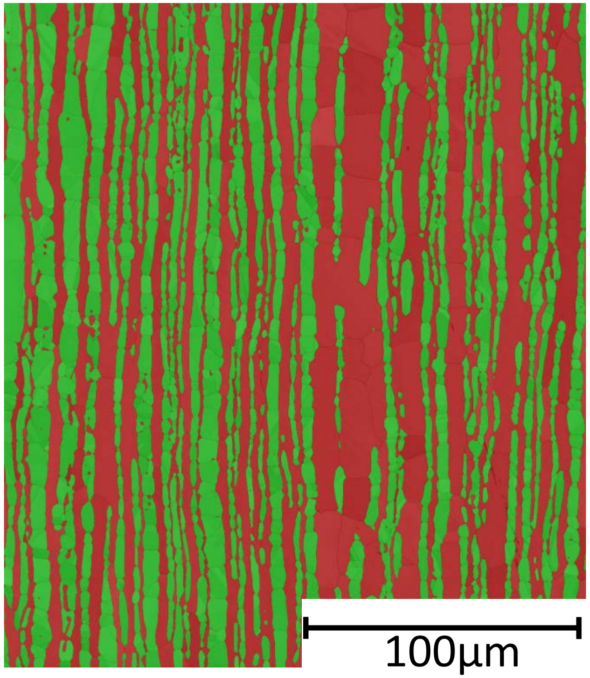
Duplex microstructure confirmed for LDX 2101

SEM



As received 2101 (duplex)
Unexposed

EBSD



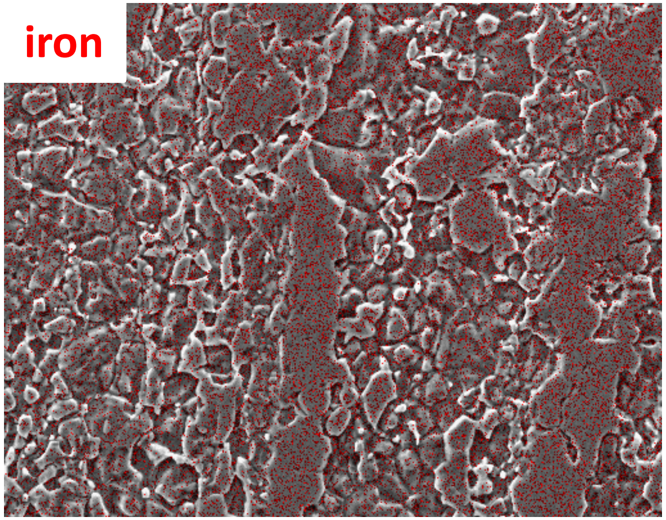
🟥 *Ferrite (54.4%)*
🟩 *Austenite (45.6%)*

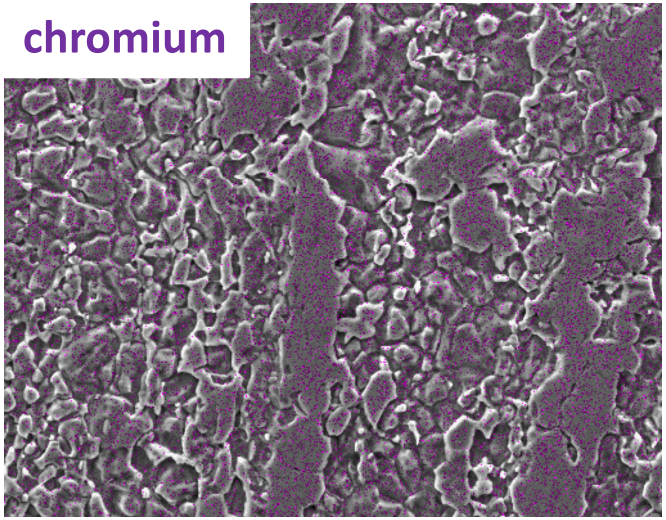
EDS

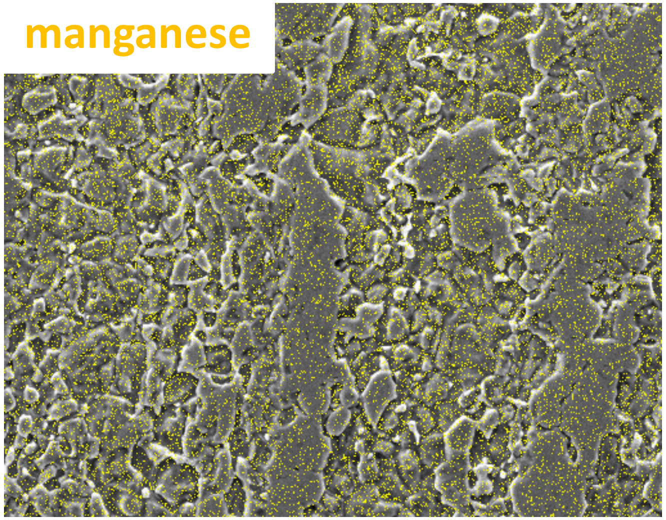
	Based on supplier (wt%)	EDS results range (wt%)
Fe	Bal.	Bal.
Cr	21.4	20.9 - 22.2
Mn	4.8	0.5 - 6.1
Ni	1.6	0.0 - 2.4
Mo	0.3	0.0 – 1.6
Cu	0.3	0.0 – 0.6

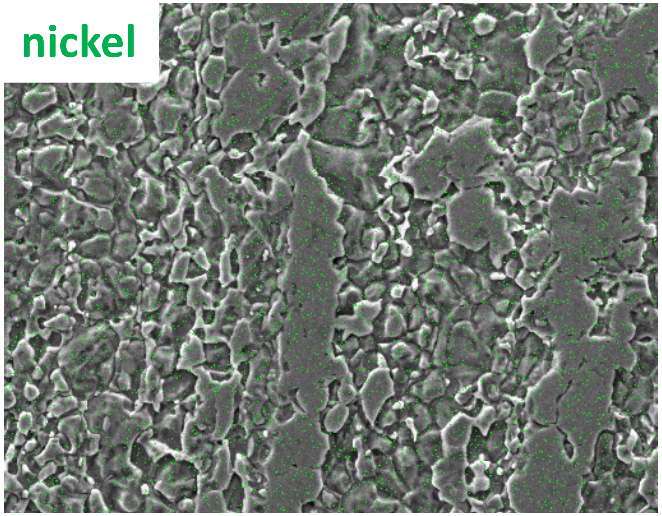
EDS mapping for LDX 2101

As received 2101 (2B)
Unexposed


iron

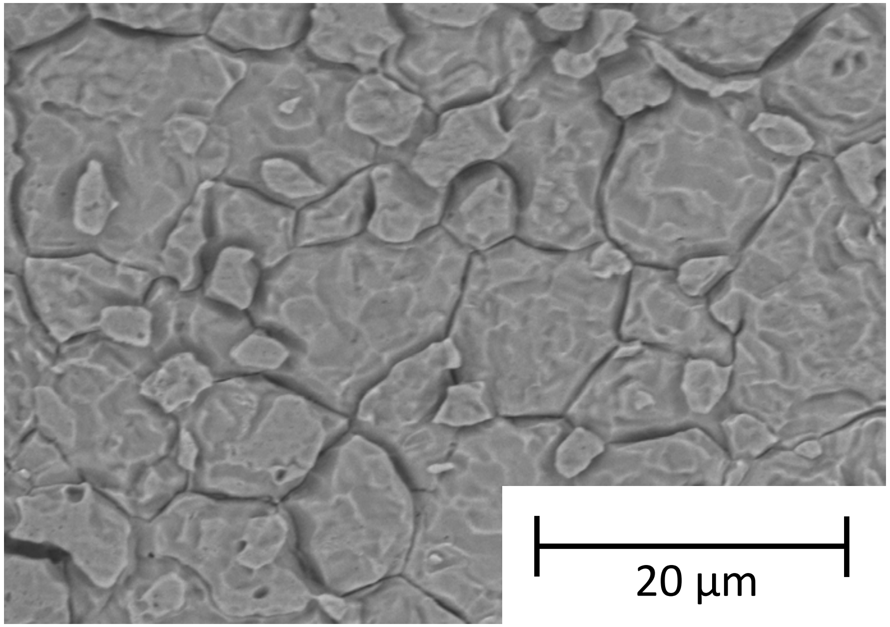

chromium


manganese

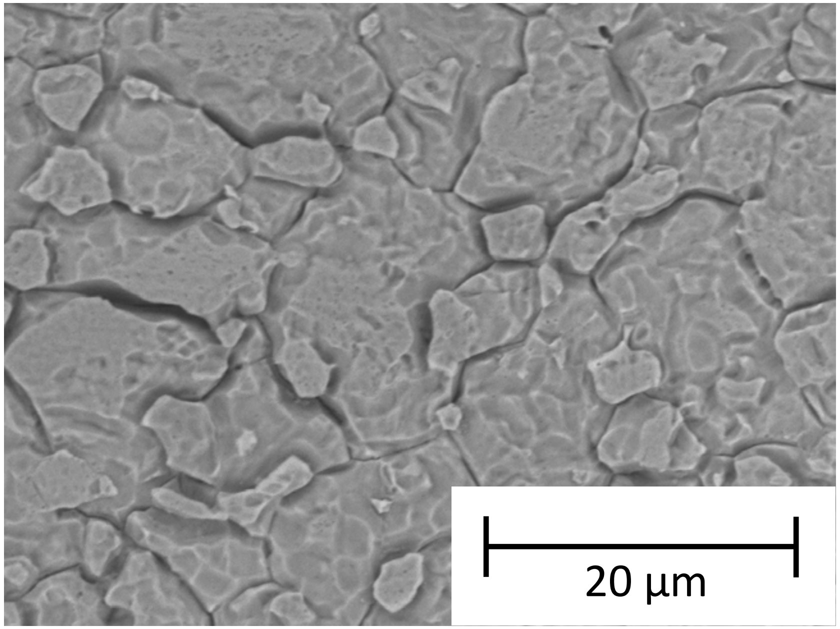

nickel

No visible changes in surface topography of grade 201 after exposure in citric acid solutions or artificial tap water.

Surface - SEM



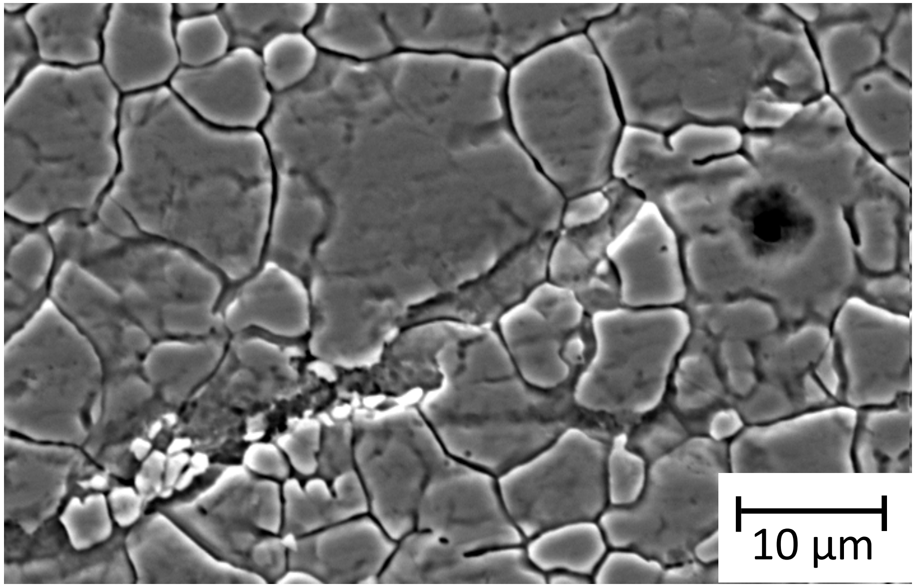
As-received 201
Unexposed



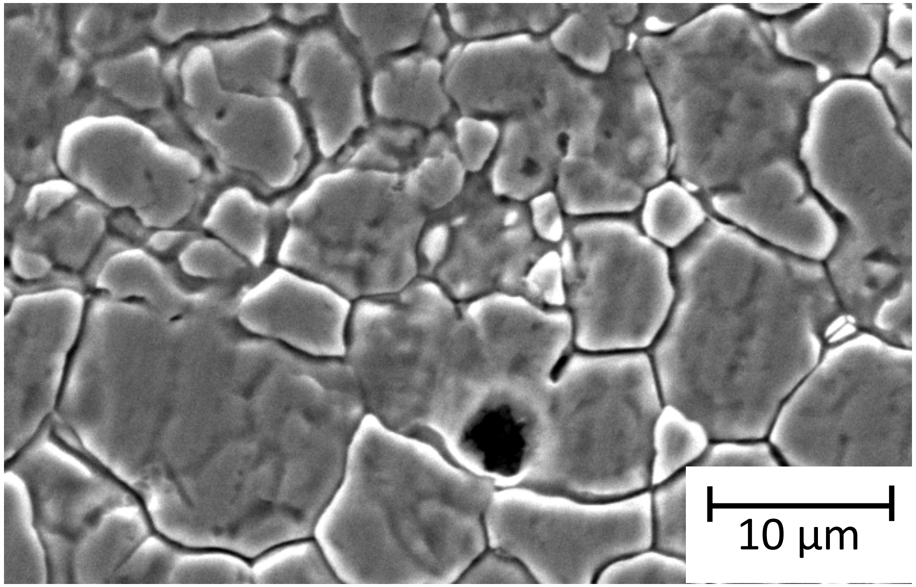
As-received 201
Citric acid pH 4.5
8 h at 70/40 °C

No visible changes in surface topography of grade 304 after exposure in citric acid solutions or tap water.

Surface - SEM

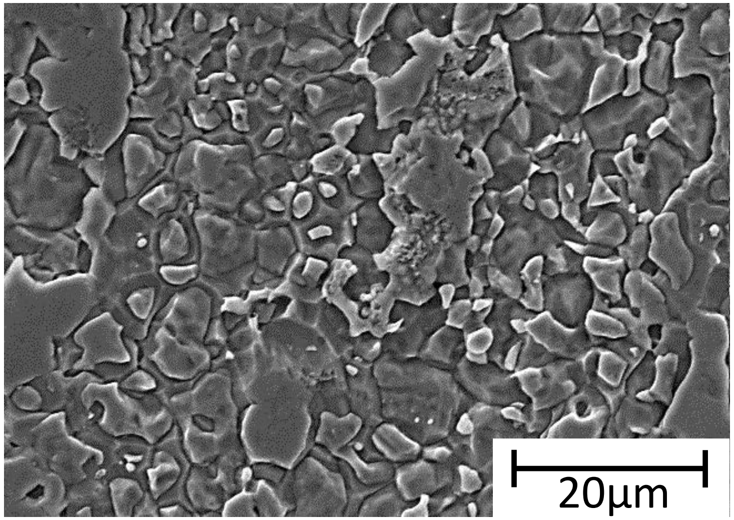


As-received 304
Unexposed

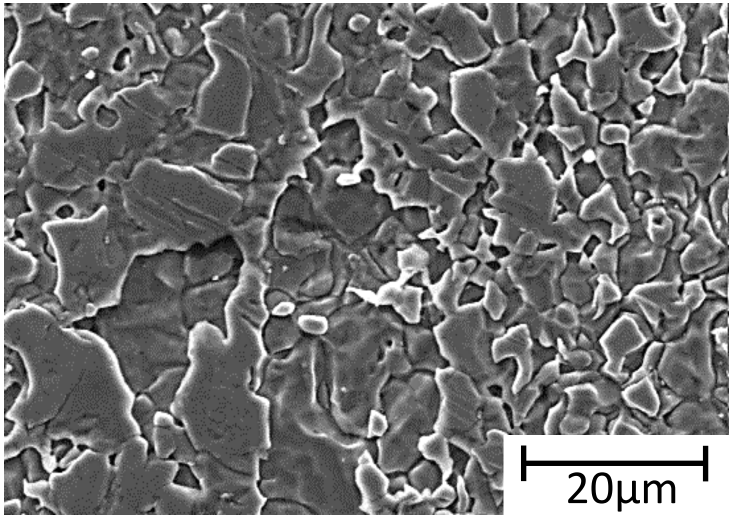


As-received 304
Citric acid pH 2.4
10 days at 70/40 ^{o}C

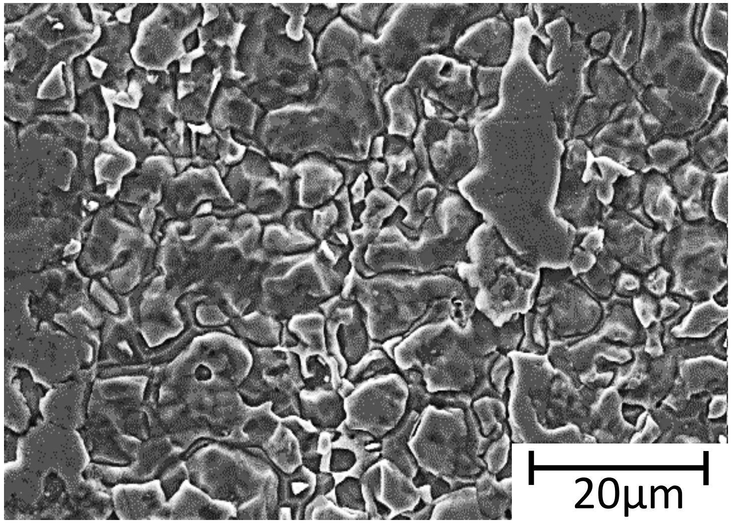
No visible changes in surface topography of grade LDX 2101 after exposure in citric acid (pH 2.4) or artificial tap water.



As received 2101
Unexposed



As received 2101
Tap water pH 7.5
240 h at 70/40^{o}C

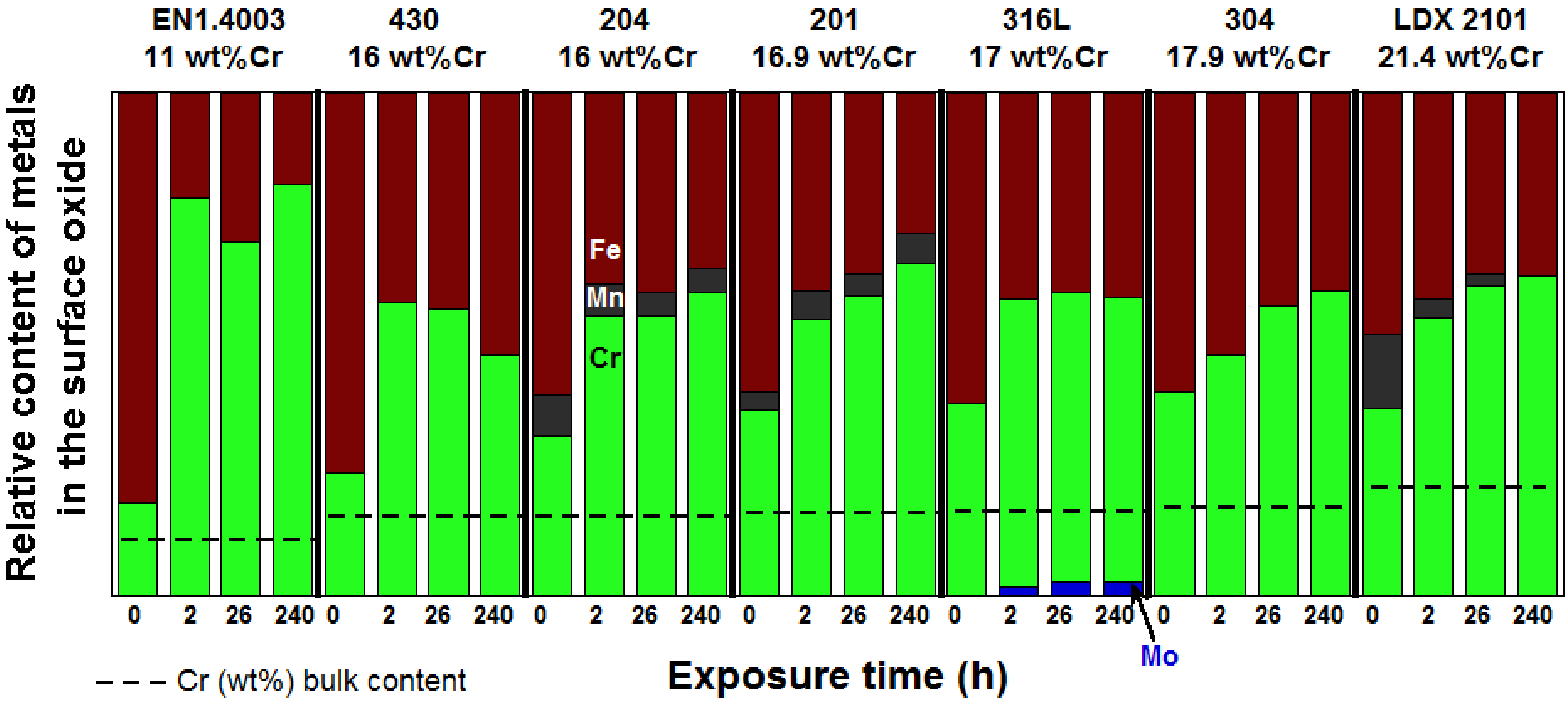


As received 2101
Citric acid pH 2.4
240 h at 70/40^{o}C

Surface enrichment of Cr for all investigated grades. Depletion of Mn from the utmost surface oxide of 2101 after exposure in citric acid (pH 2.4).

Surface oxide – XPS

Citric acid pH 2.4, as-received, 70/40 °C, CoE protocol

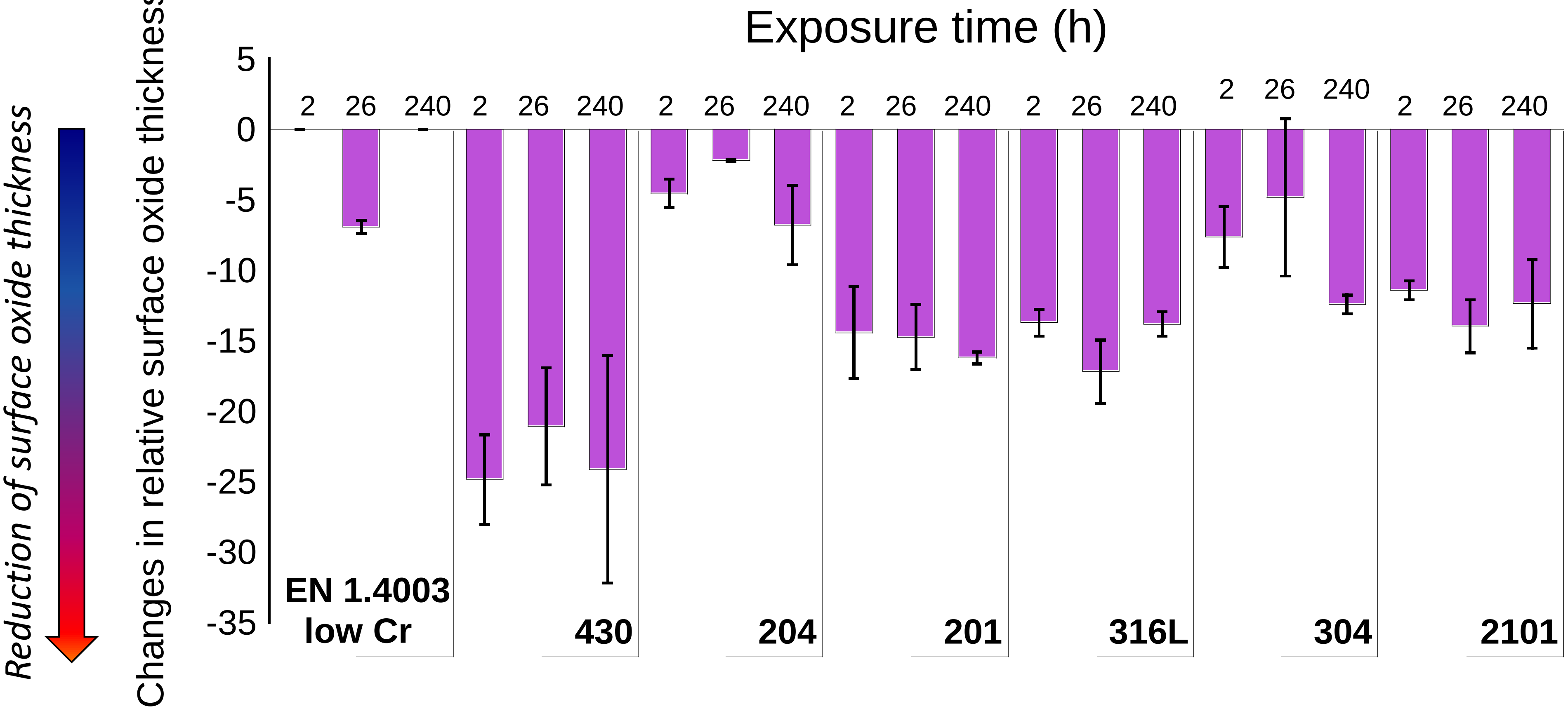


ROYAL INSTITUTE
OF TECHNOLOGY

Reduction in surface oxide thickness for all investigated grades after exposure to citric acid (pH 2.4). No clear changes for EN1.4003.

Citric acid pH 2.4, as-received, 70/40 °C, CoE protocol

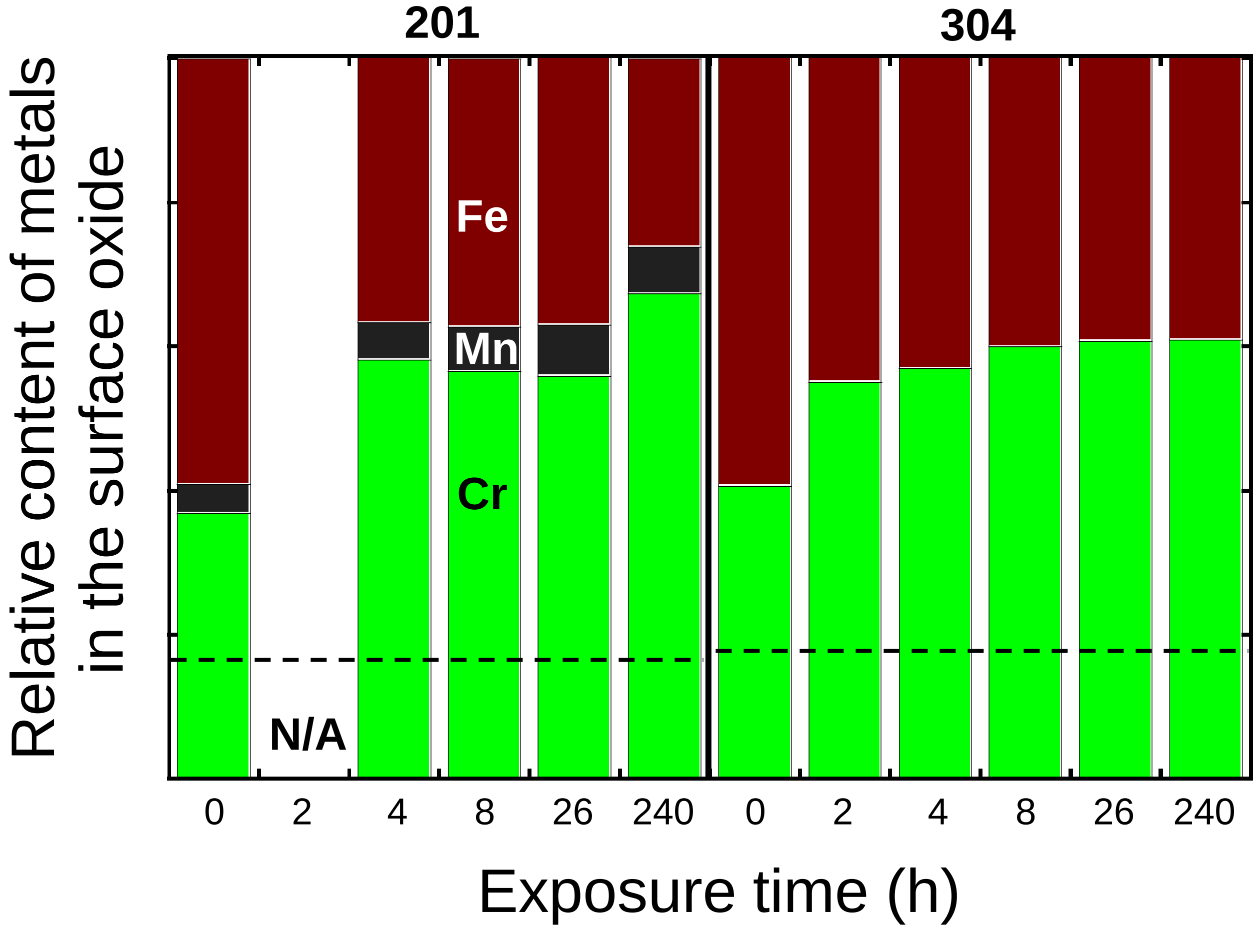
Surface oxide – XPS



Chromium enrichment of the surface oxide of 201 and 304 after exposure in citric acid (pH 4.5).

Surface oxide – XPS

Citric acid pH 4.5, as-received, 70/40 °C



- - - Cr (wt%) bulk content

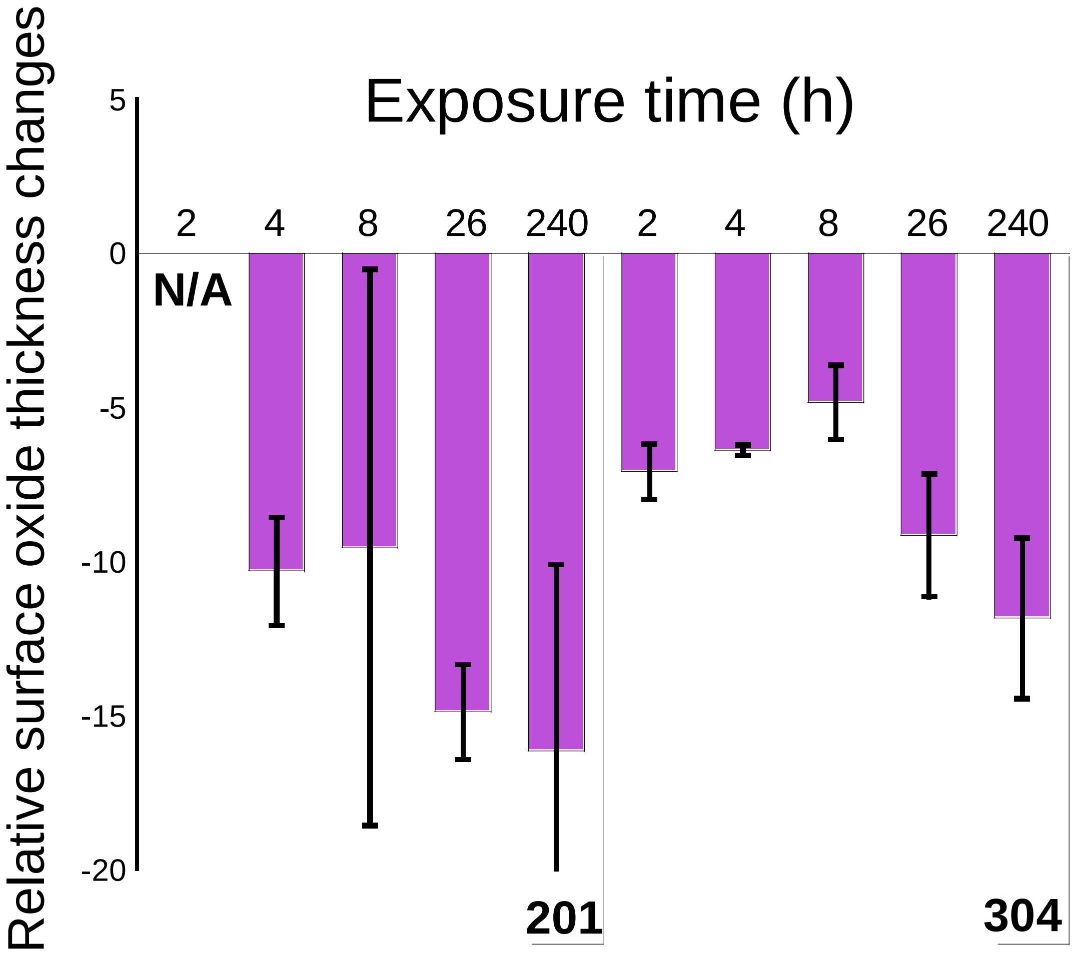
N/A= no data available

ROYAL INSTITUTE OF TECHNOLOGY

Reduction in surface oxide thickness for grades 201 and 304 after exposures in citric acid (pH 4.5).

Surface oxide – XPS

Citric acid pH 4.5, as-received, 70/40 °C

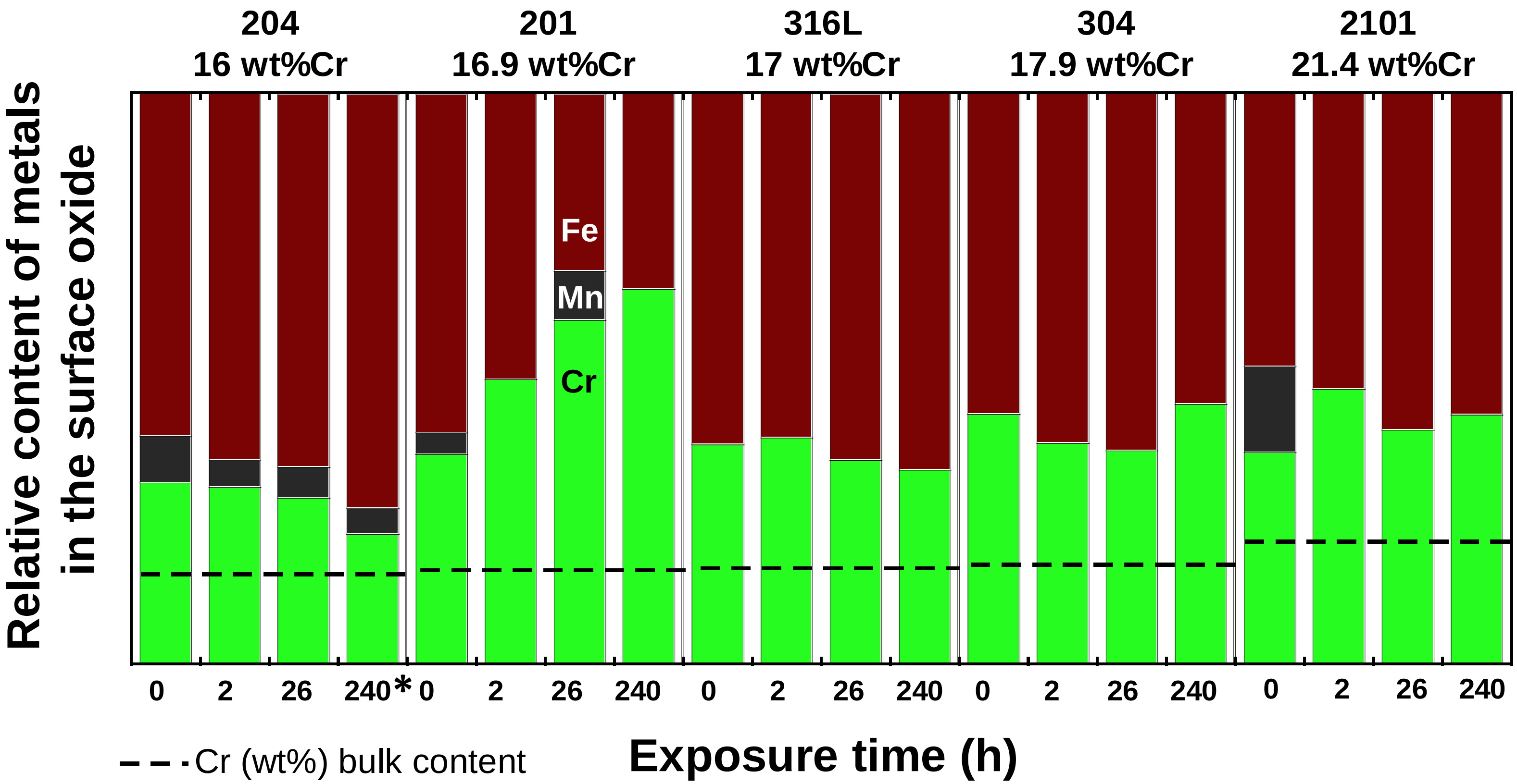


N/A= no data available

Surface enrichment of Cr for grade 201 and complete Mn depletion from the surface oxide for grade 2101 after exposure in artificial tap water (pH 7.5). No changes observed for grades 204, 304, and 316L.

Surface oxide – XPS

Artificial tap water pH 7.5, as-received, 70/40 °C, CoE protocol

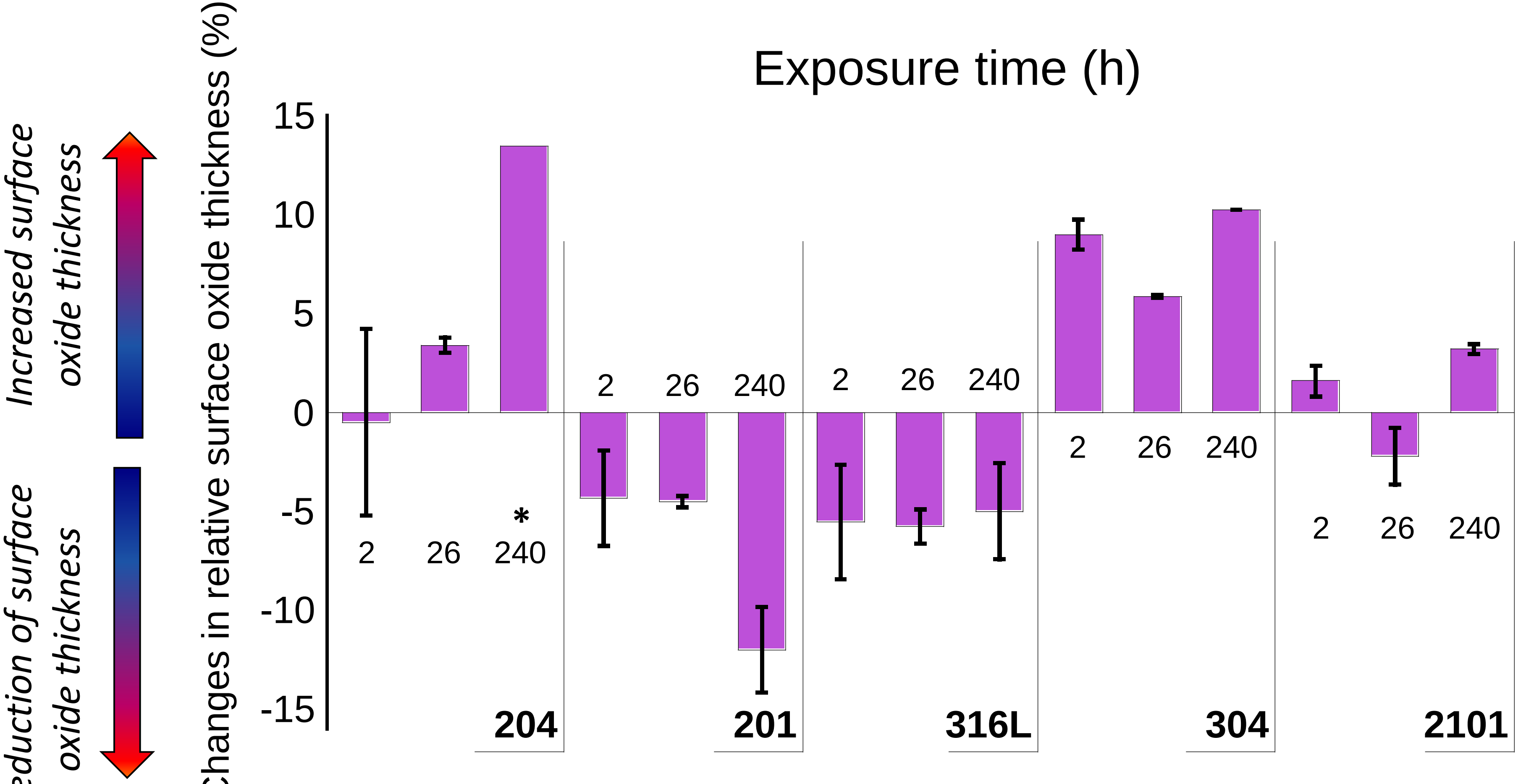


** based on one measurement*

Only minor or no changes in oxide thickness upon exposure in artificial tap water.

Surface oxide – XPS

Artificial tap water pH 7.5, as-received, 70/40 °C, CoE protocol



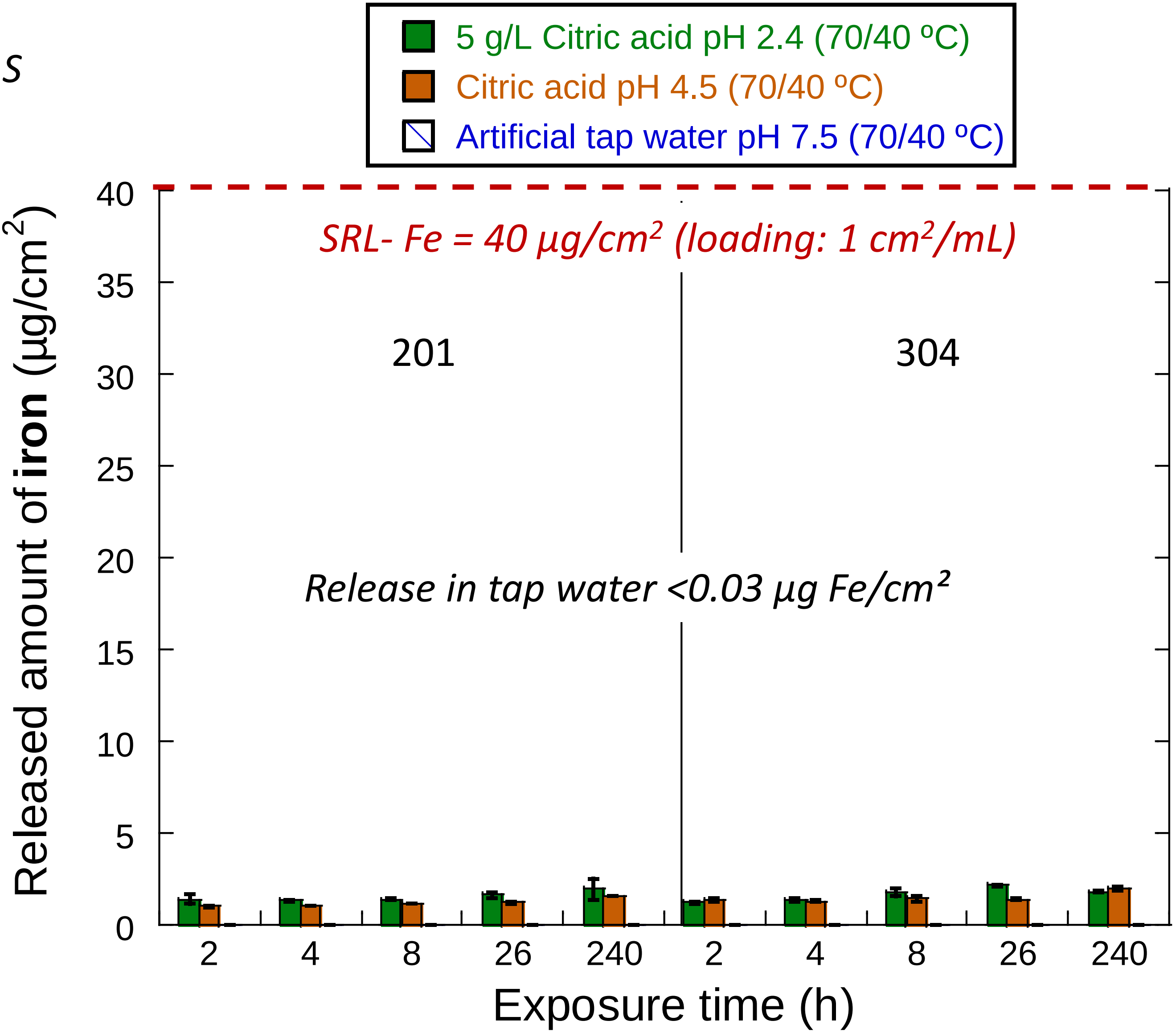
** based on one measurement*

Citric acid (pH 2.4) was the most aggressive test solution.

ROYAL INSTITUTE OF TECHNOLOGY

Metal release-AAS

As-received



SRL- Fe = 40 µg/cm² (loading: 1 cm²/mL)

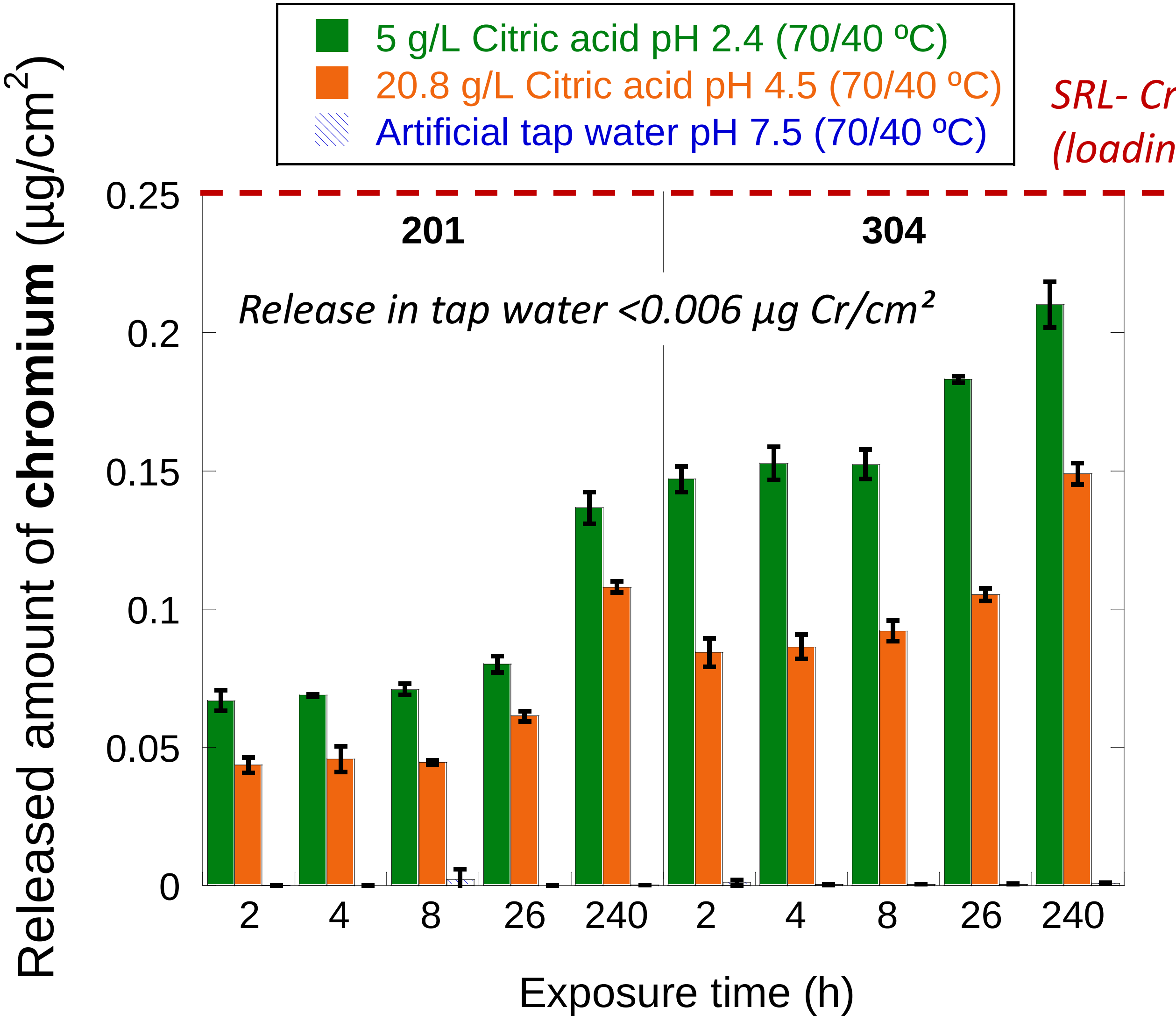
Release in tap water <0.03 µg Fe/cm²

Citric acid (pH 2.4) was the most aggressive test solution-cont.

ROYAL INSTITUTE OF TECHNOLOGY

Metal release-AAS

As-received



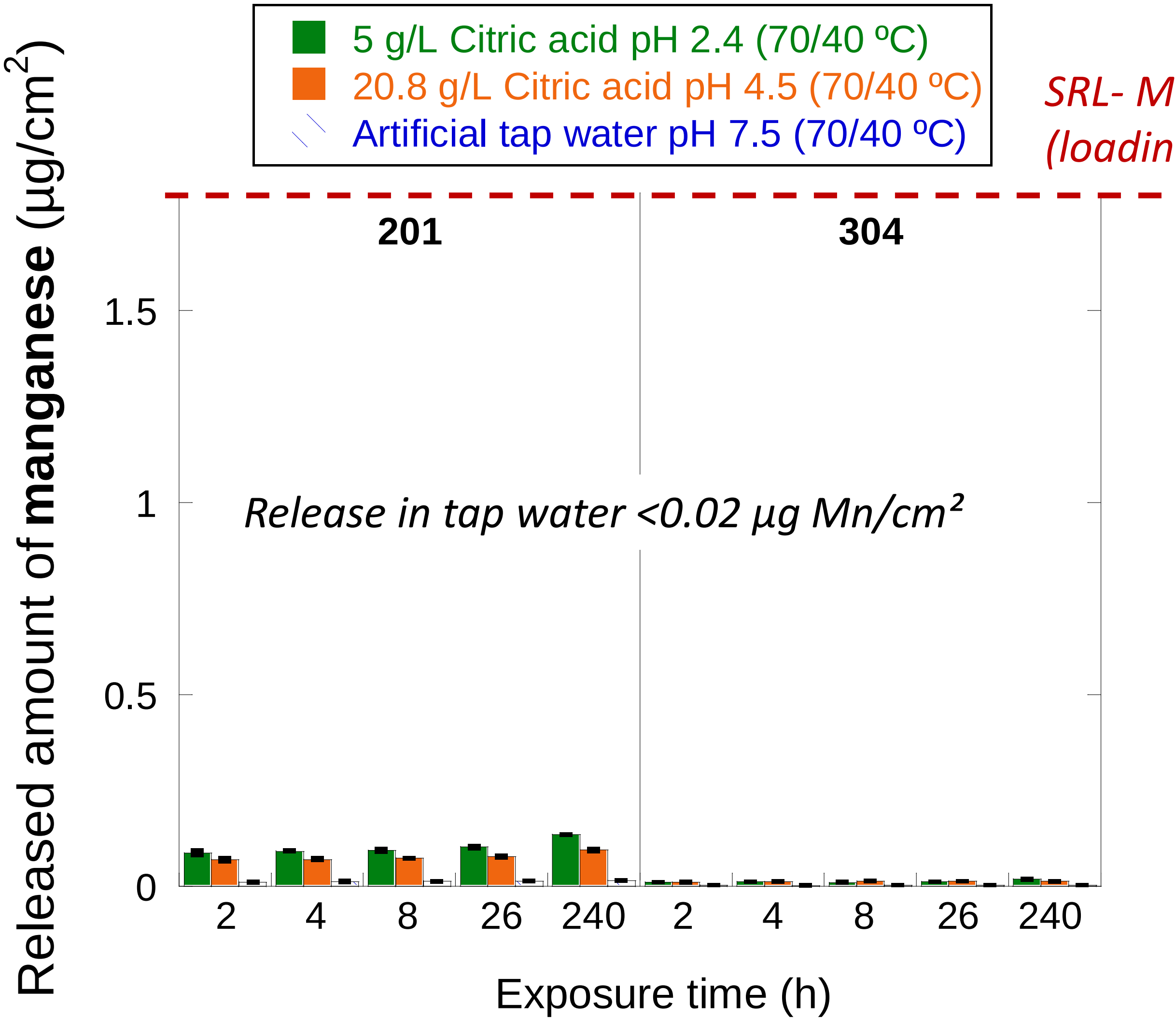
Release in tap water <0.006 µg Cr/cm²

SRL- Cr = 0.25 µg/cm²
(loading: 1 cm²/mL)

Citric acid (pH 2.4) was the most aggressive test solution-cont.

Metal release-AAS

As-received



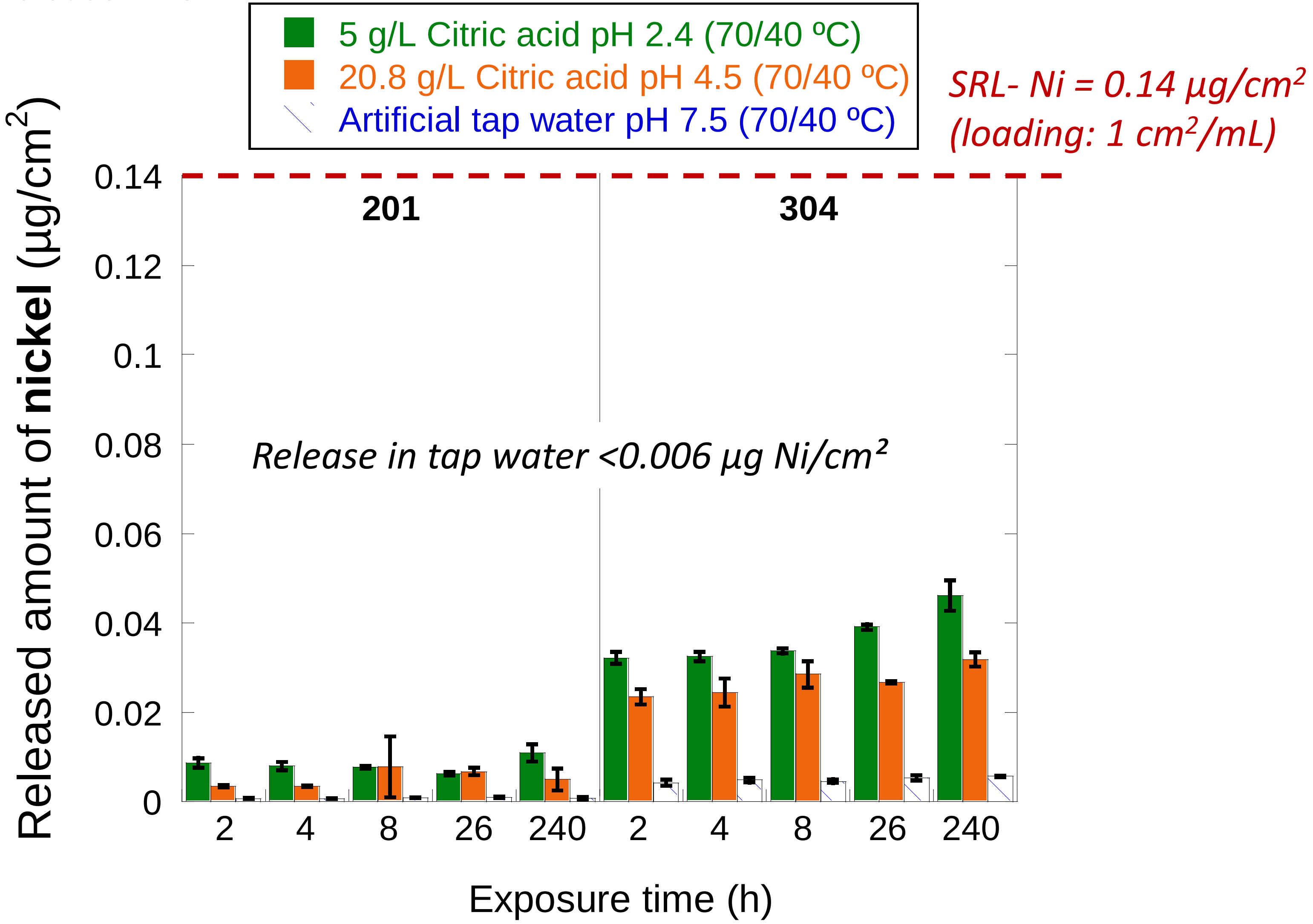
Release in tap water <0.02 µg Mn/cm²

SRL- Mn = 1.8 µg/cm^2
(loading: 1 cm^2/mL)

Citric acid (pH 2.4) was the most aggressive test solution-cont.

Metal release-AAS

As-received

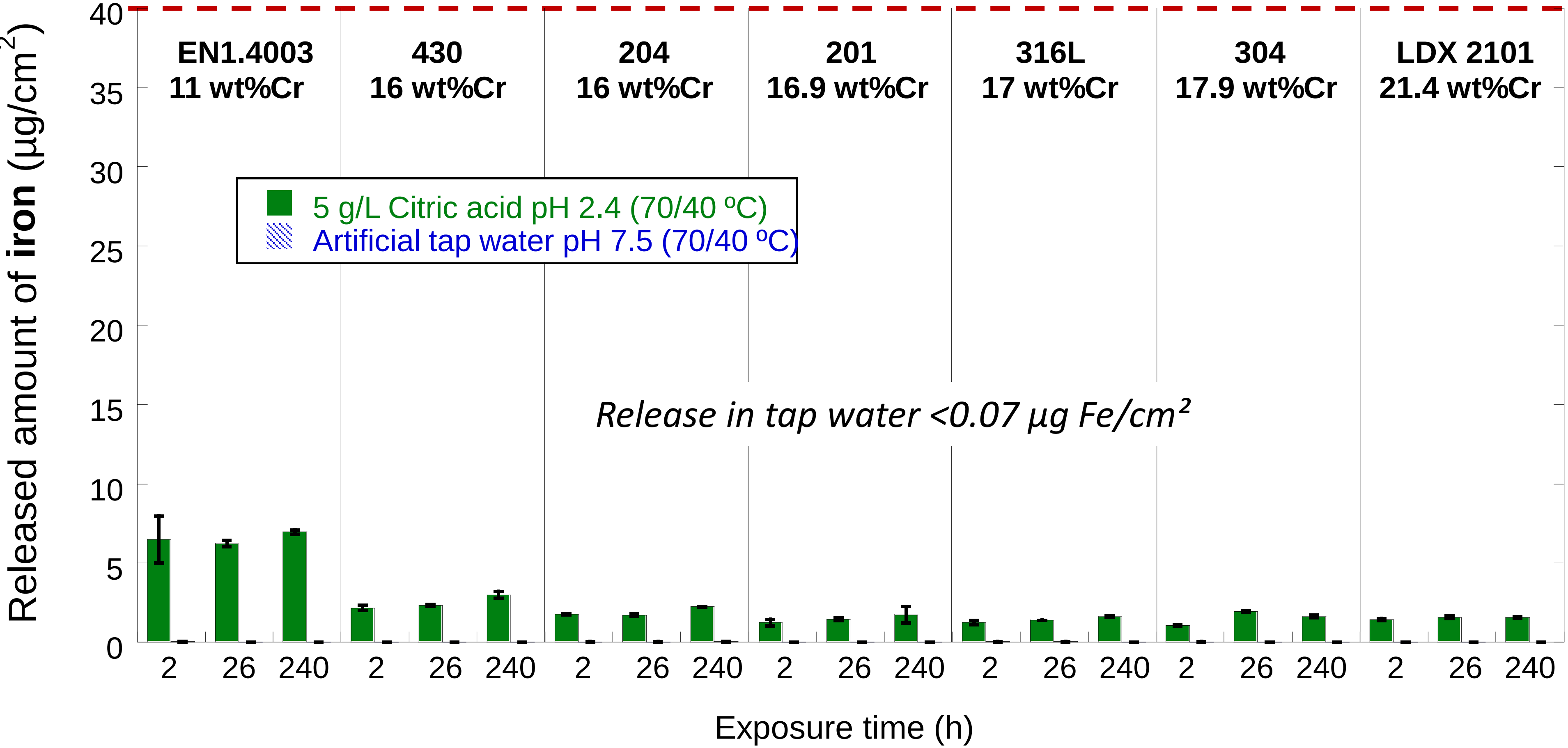


More Fe released from grade EN1.4003 (low Cr) in citric acid (pH 2.4) compared with the other grades.

Metal release-AAS

As-received

SRL- Fe = 40 µg/cm² (loading: 1 cm²/mL)

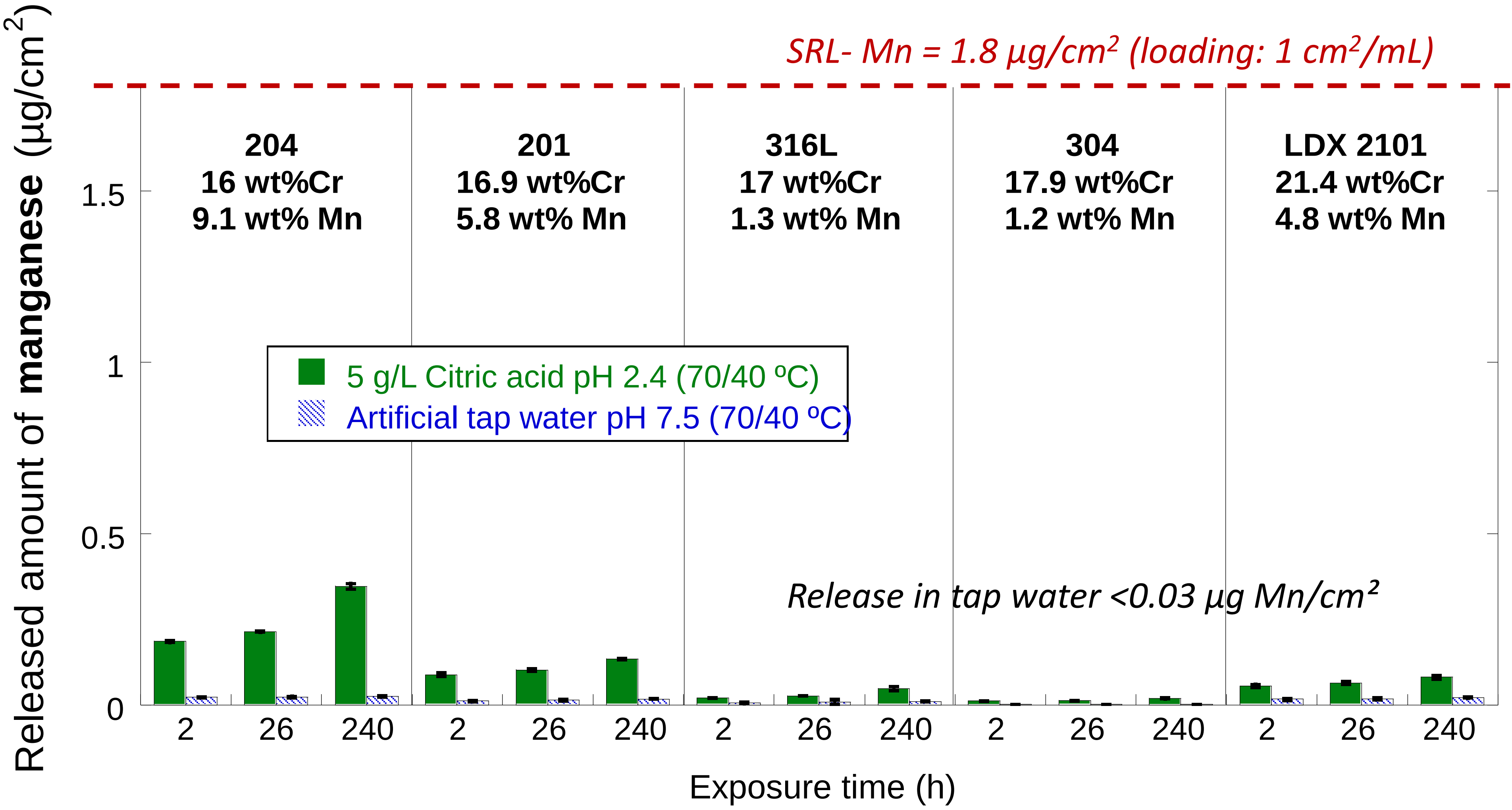


Release in tap water <0.07 µg Fe/cm²

More Mn released from grade 204 compared with the other grades. Released amounts of Mn proportional to the Mn bulk alloy content.

Metal release-AAS

As-received

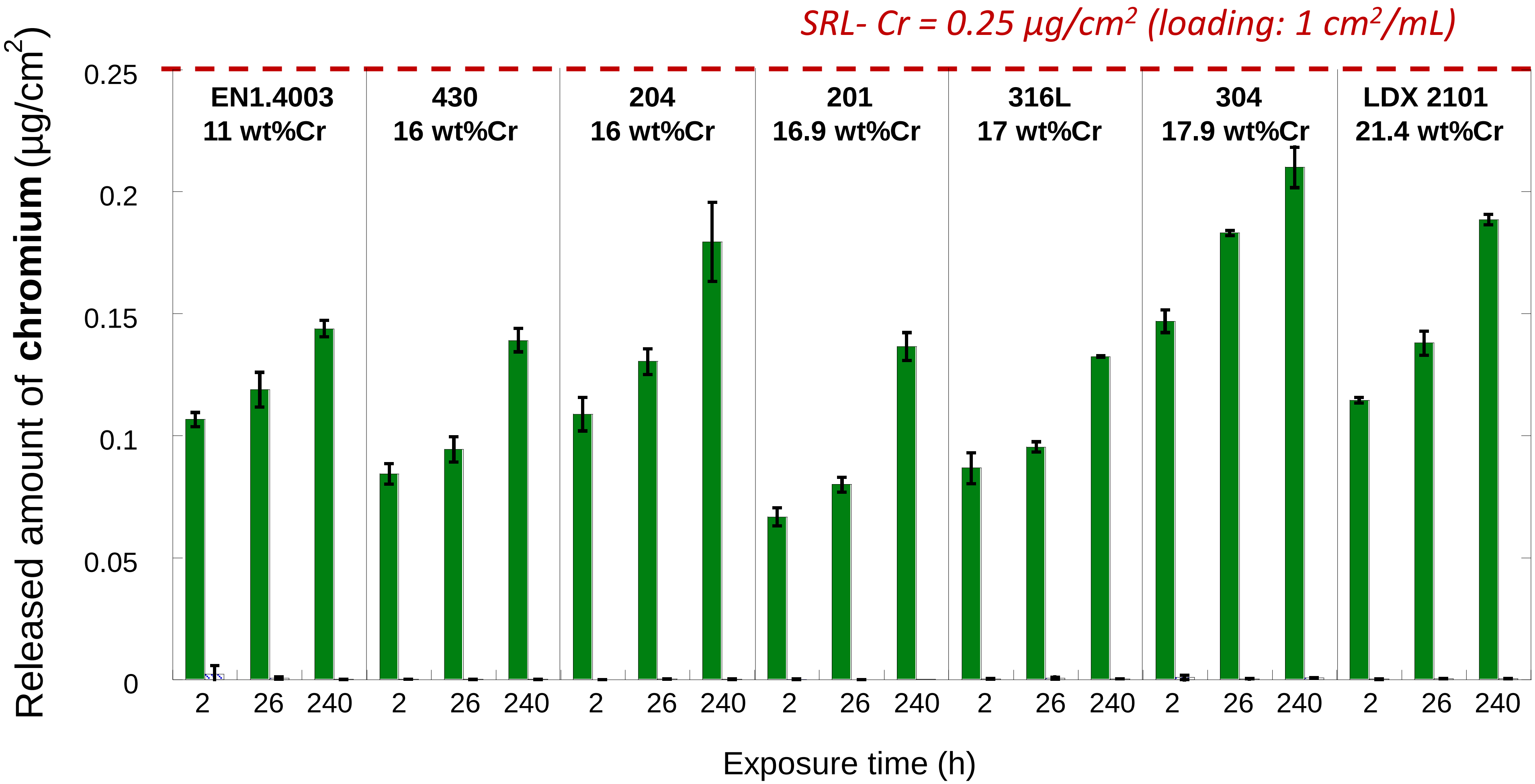


More Cr released from grade 304 in citric acid (pH 2.4) compared with the other investigated grades.

Metal release-AAS

As-received

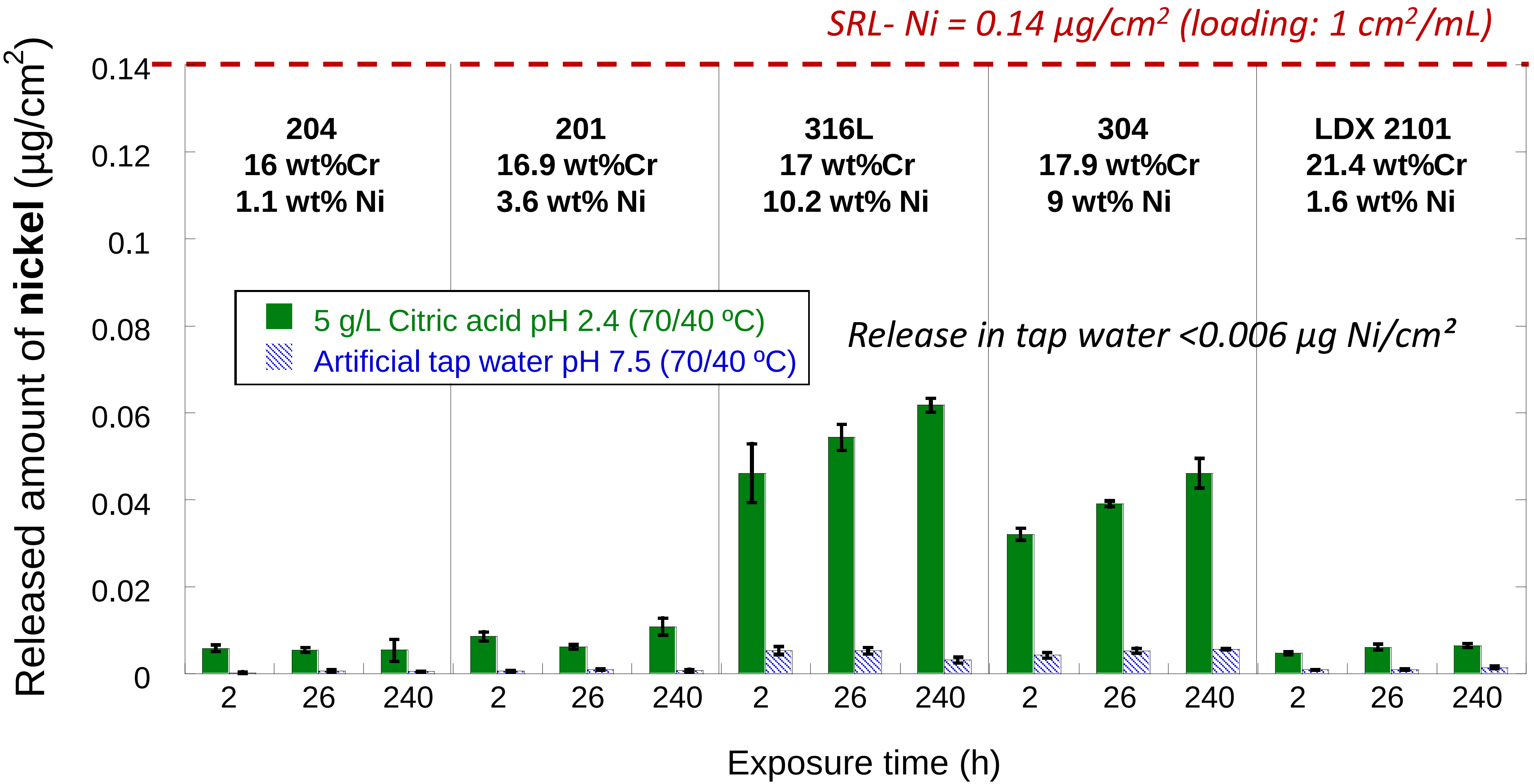
Release in tap water <0.006 µg Cr / cm²



More Ni released from grades 316L and 304 in both test solutions compared with the other investigated grades.

Metal release-AAS

As-received

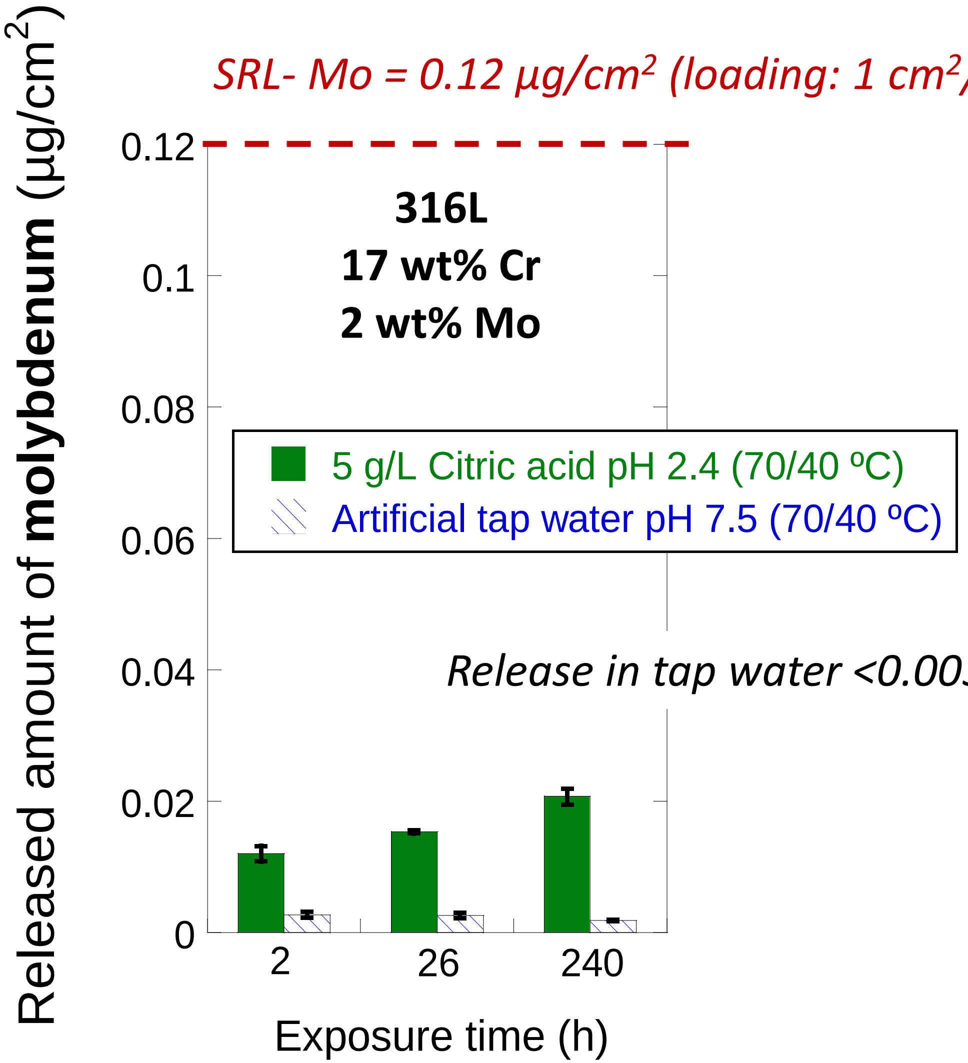


More Mo released from grade 316L in citric acid (pH 2.4) compared with artificial tap water (pH 7.5).

Metal release-AAS

As-received

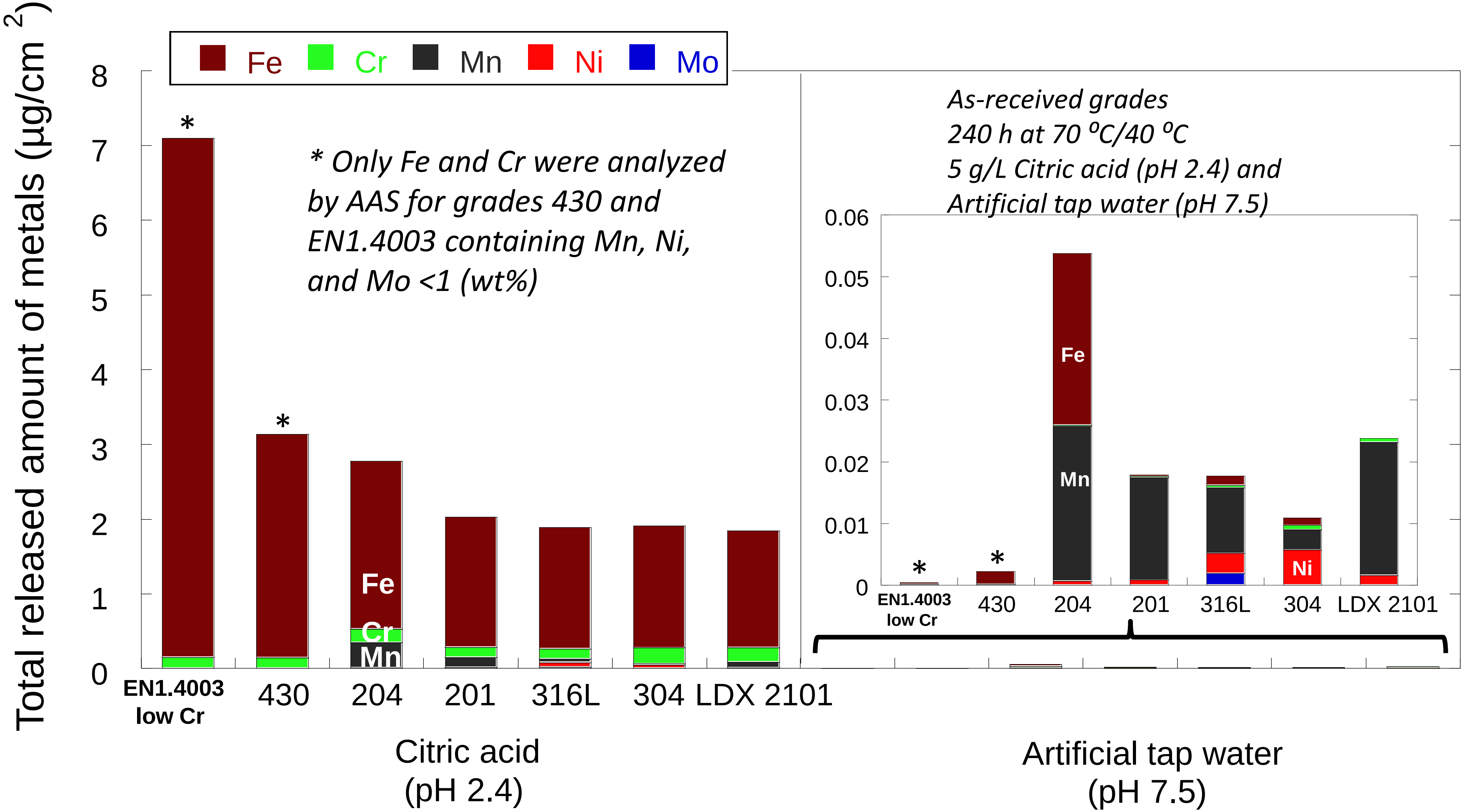
SRL- Mo = 0.12 µg/cm² (loading: 1 cm²/mL)



Release in tap water <0.003 µg Mo/cm²

Most metals released from grade EN1.4003 (low Cr) upon exposure in citric acid (pH 2.4).

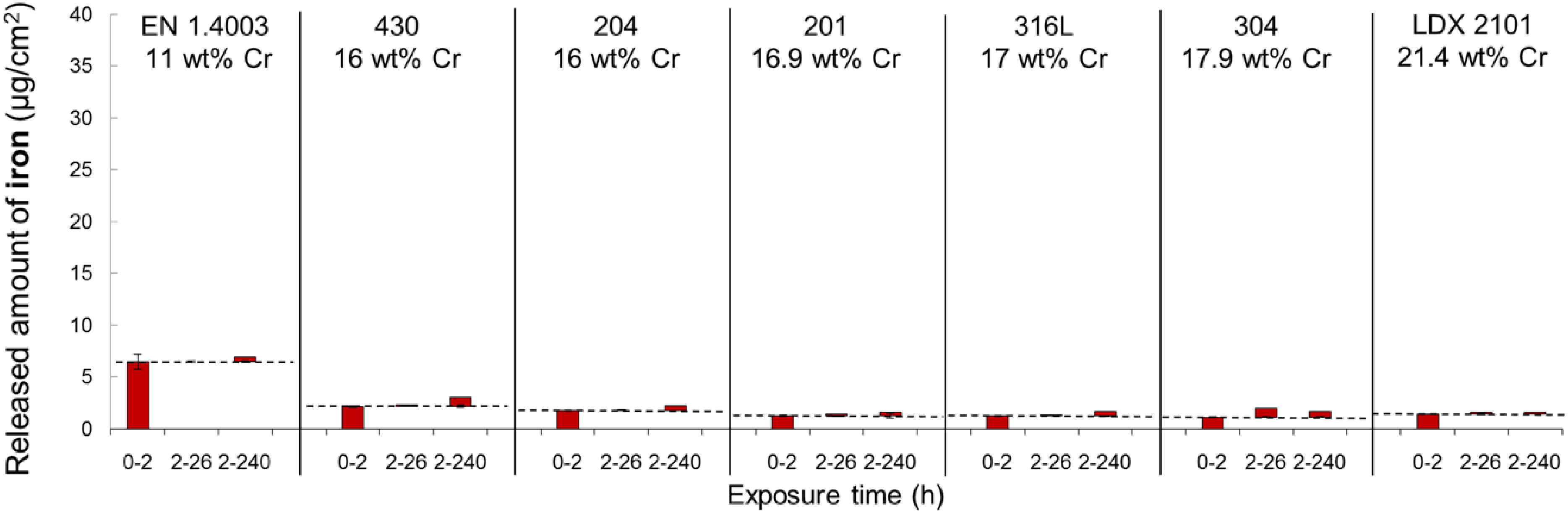
Metal release-AAS



** Only Fe and Cr were analyzed by AAS for grades 430 and EN1.4003 containing Mn, Ni, and Mo <1 (wt%)*

As-received grades
240 h at 70 °C/40 °C
5 g/L Citric acid (pH 2.4) and
Artificial tap water (pH 7.5)

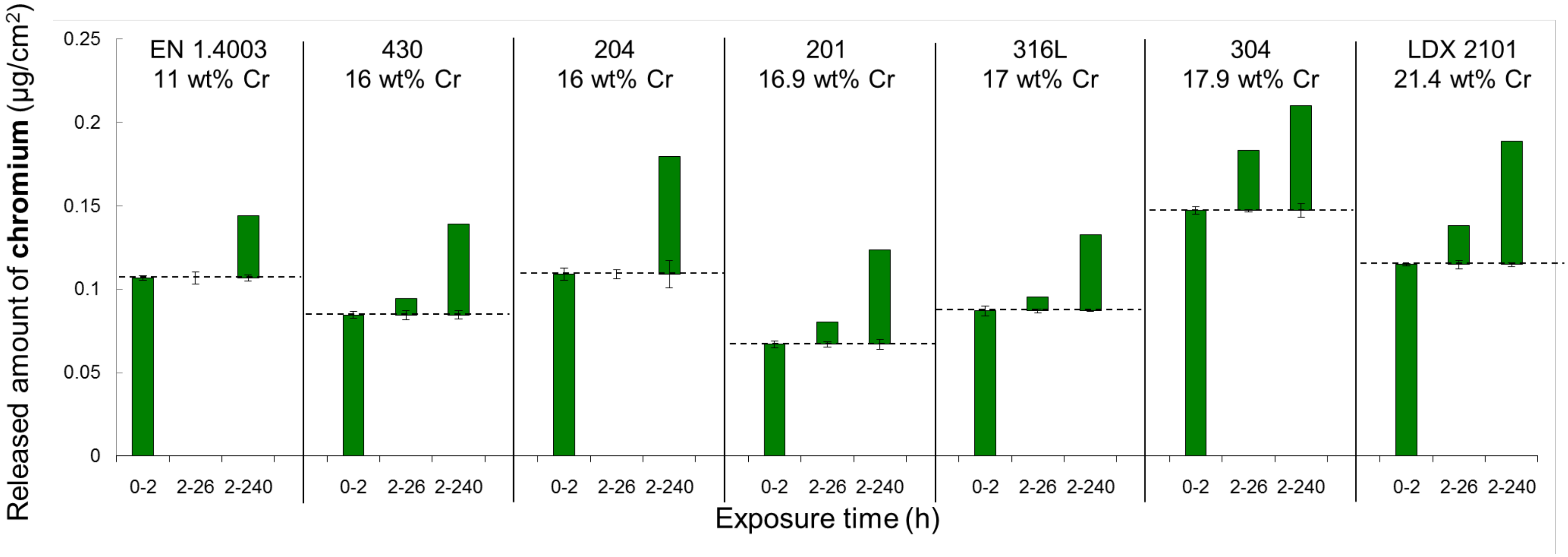
Most Fe released into citric acid (pH 2.4) during the first 2 hours of exposure.



As-received surfaces

Exposure in citric acid (pH 2.4) for 2 h at 70 °C , 2 h at 70 °C followed by 24 h at 40 °C, and 2 h at 70 °C followed by 238 h at 40 °C.

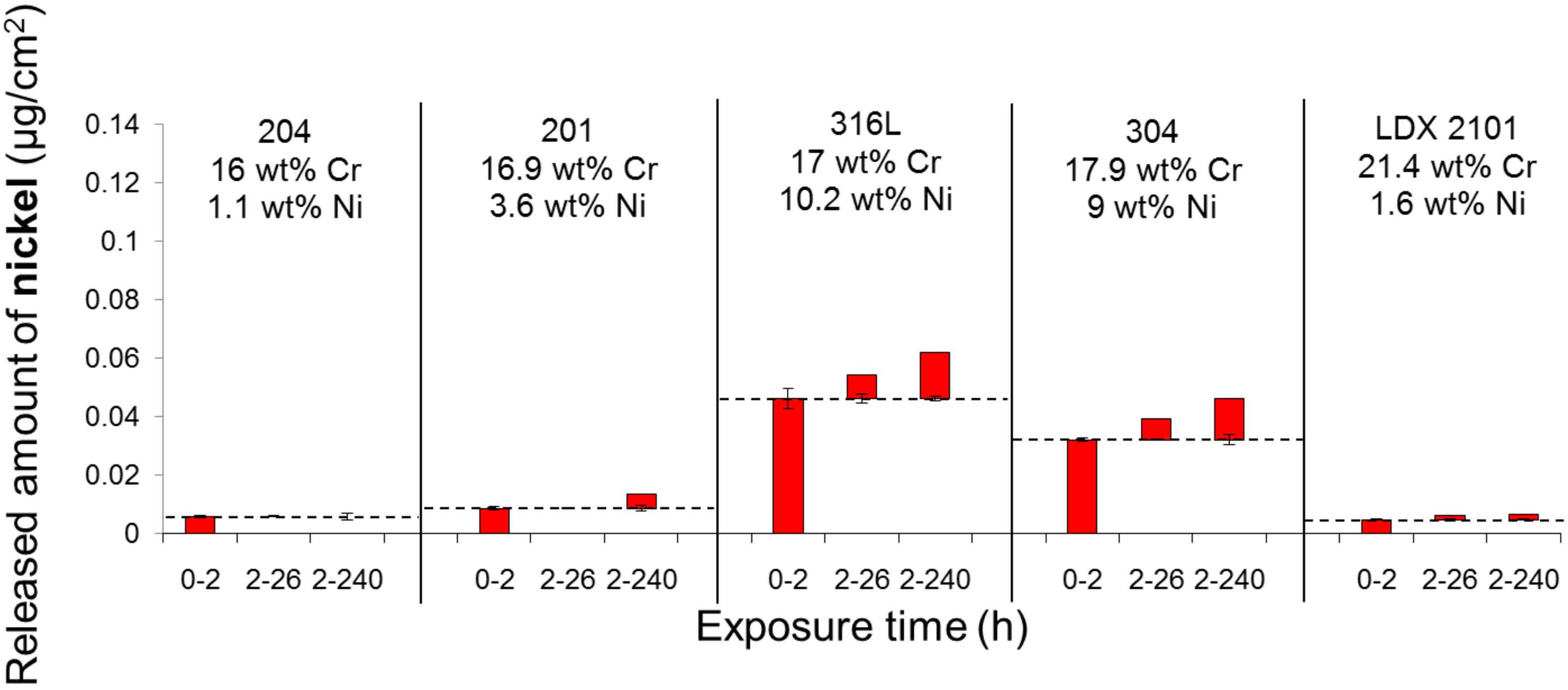
Most Cr released into citric acid (pH 2.4) during the first 2 hours of exposure.



As-received surfaces

Exposure in citric acid (pH 2.4) for 2 h at 70 °C , 2 h at 70 °C followed by 24 h at 40 °C, and 2 h at 70 °C followed by 238 h at 40 °C.

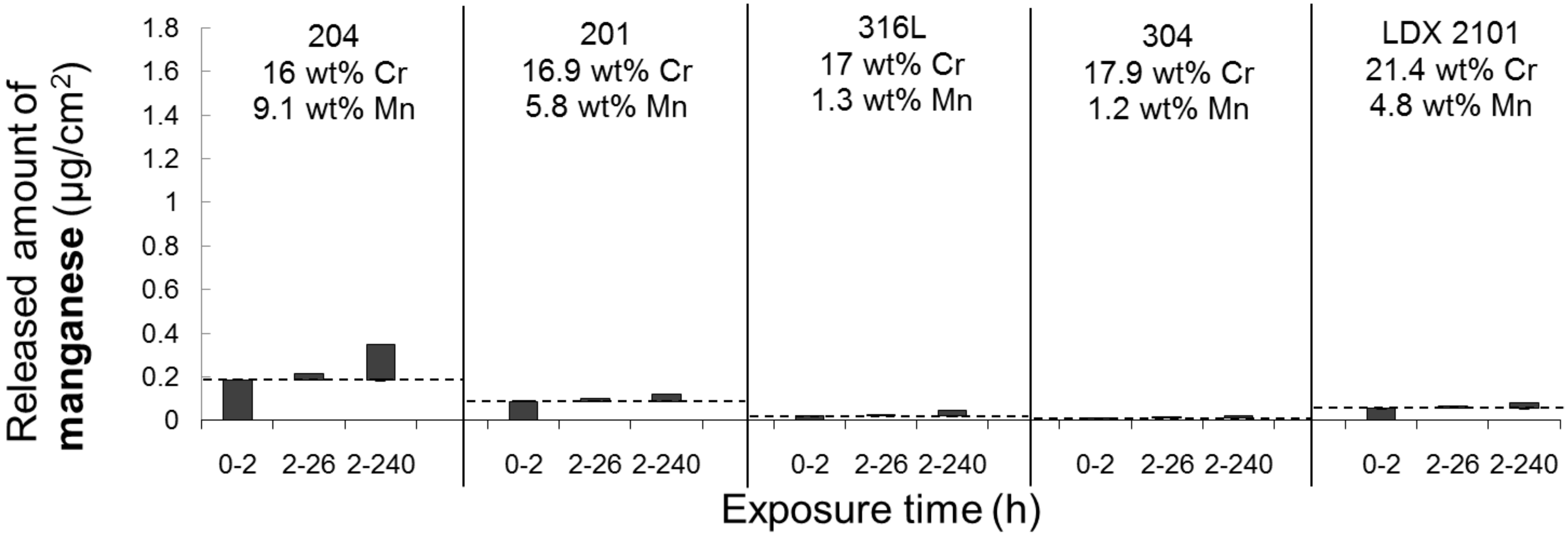
Most Ni released into citric acid (pH 2.4) during the first 2 hours of exposure.



As-received surfaces

Exposure in citric acid (pH 2.4) for 2 h at 70 °C , 2 h at 70 °C followed by 24 h at 40 °C, and 2 h at 70 °C followed by 238 h at 40 °C.

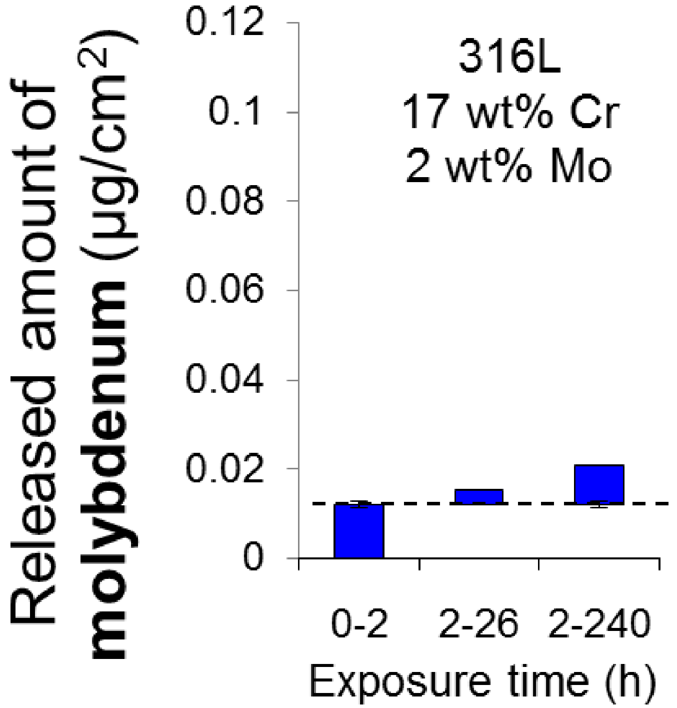
Most Mn released into citric acid (pH 2.4) during the first 2 hours of exposure.



As-received surfaces

Exposure in citric acid (pH 2.4) for 2 h at 70 °C , 2 h at 70 °C followed by 24 h at 40 °C, and 2 h at 70 °C followed by 238 h at 40 °C.

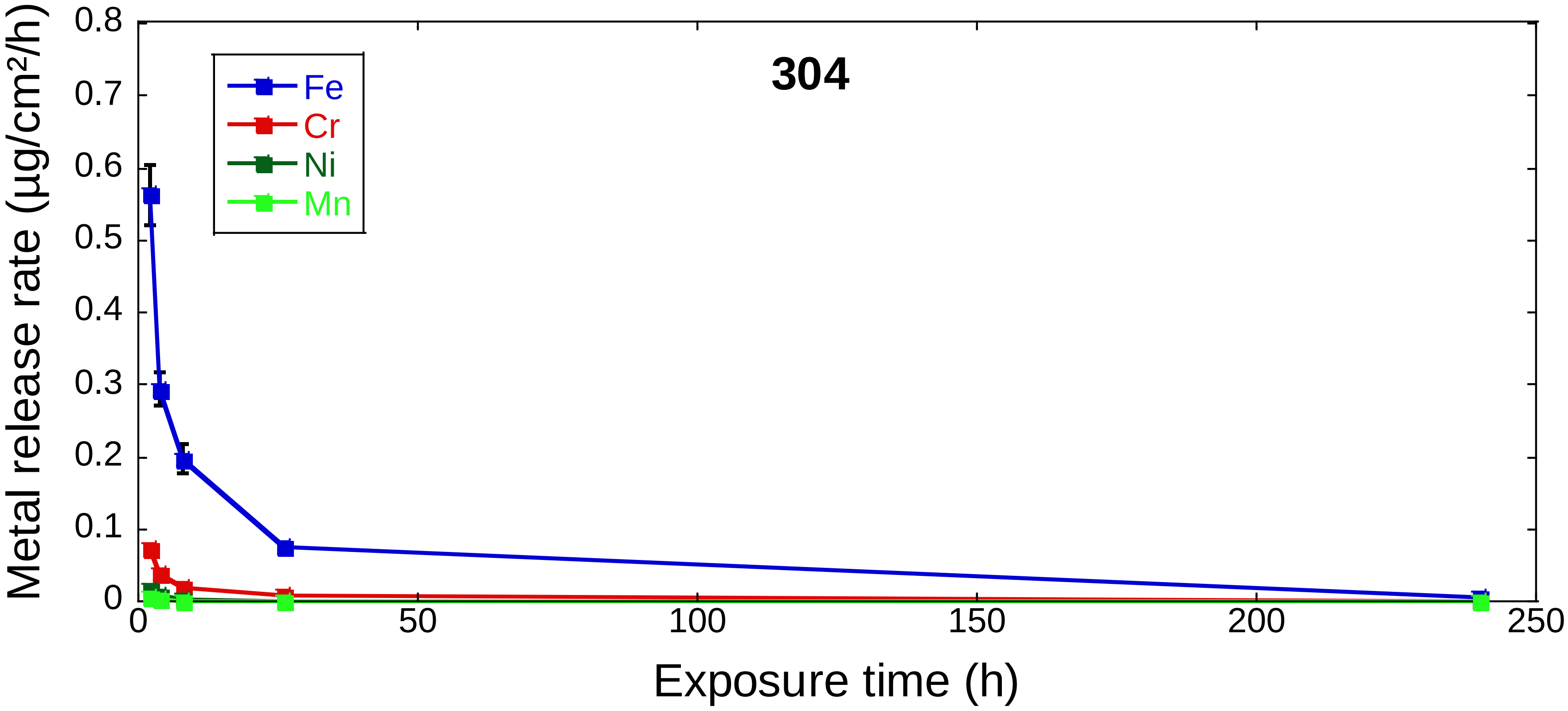
Most Mo released into citric acid (pH 2.4) during the first 2 hours of exposure.



As-received surfaces

Exposure in citric acid (pH 2.4) for 2 h at 70 °C , 2 h at 70 °C followed by 24 h at 40 °C, and 2 h at 70 °C followed by 238 h at 40 °C.

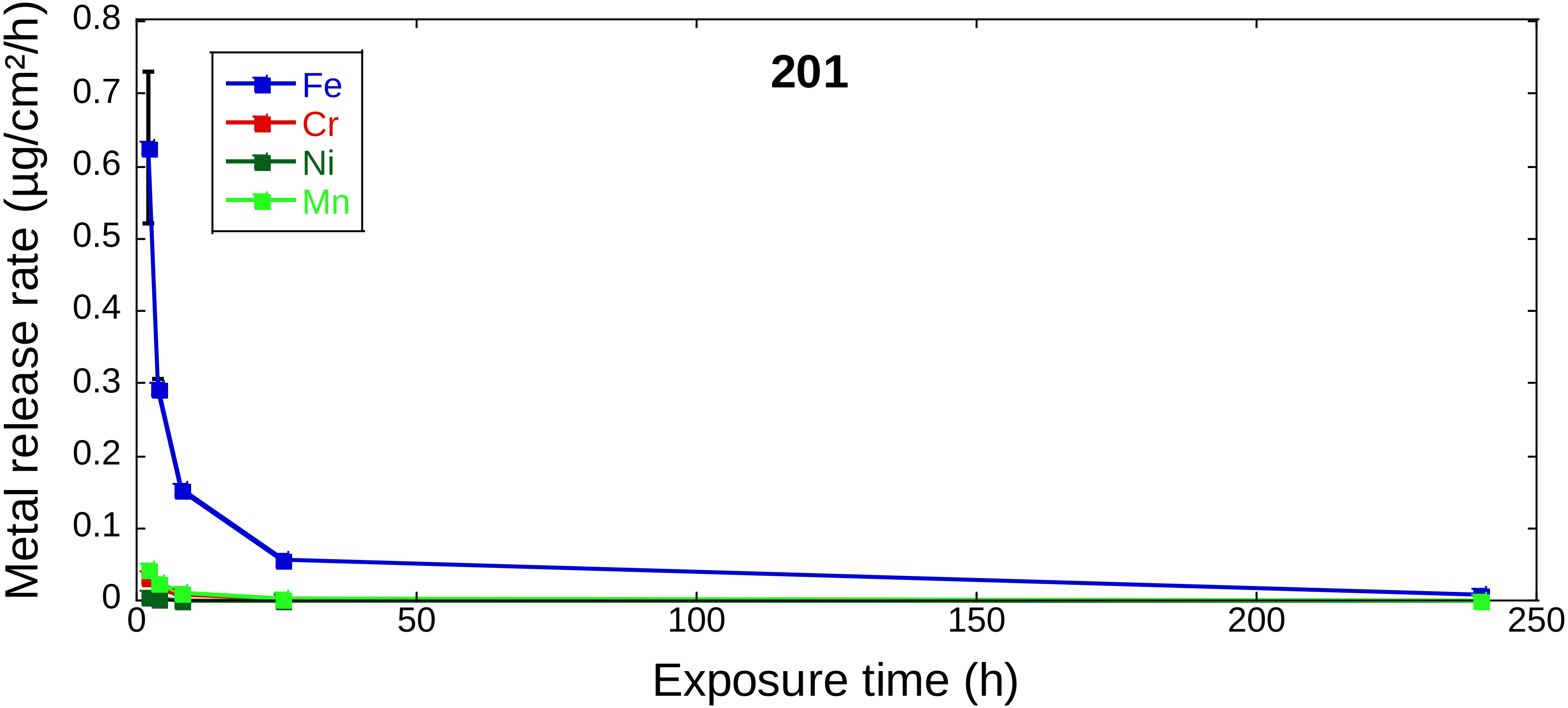
Lower release rates of all metals with time for grade 304.



As-received surface – 304 (2B)

Exposure in citric acid (pH 2.4) for 2 h at 70 °C , 2 h at 70 °C followed by 24 h at 40 °C, and 2 h at 70 °C followed by 238 h at 40 °C.

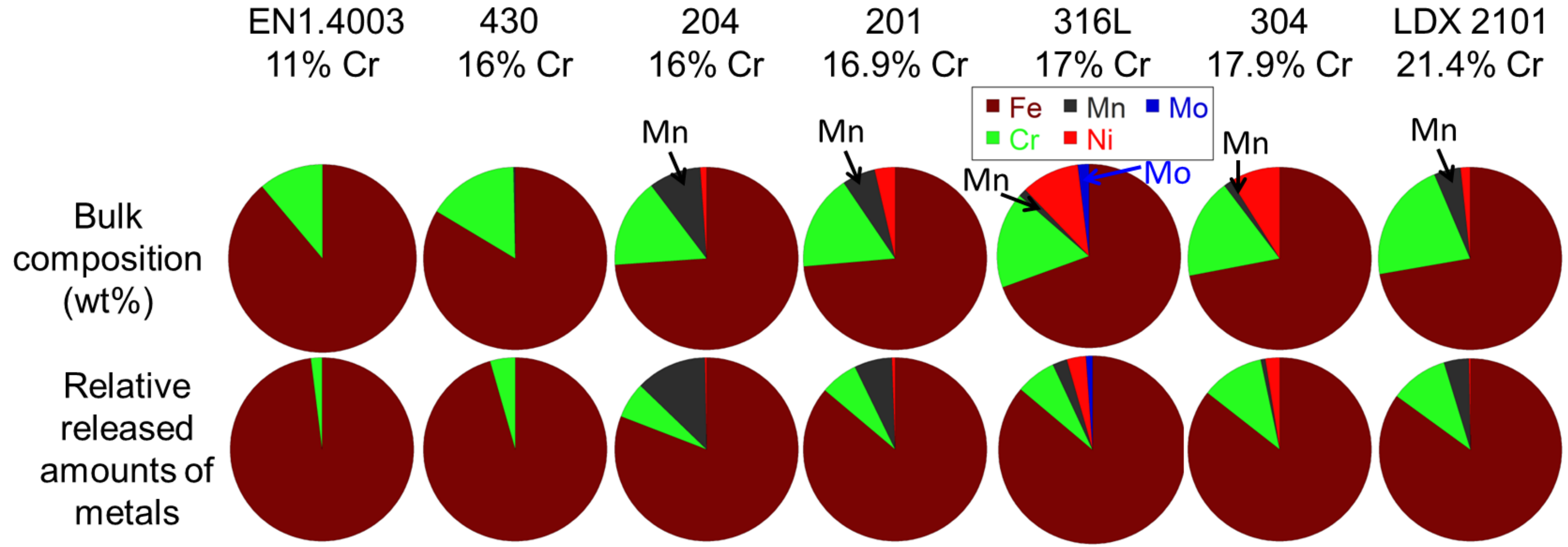
Lower release rates of all metals with time for grade 201.



As-received surface – 201 (2D)

Exposure in citric acid (pH 2.4) for 2 h at 70 °C , 2 h at 70 °C followed by 24 h at 40 °C, and 2 h at 70 °C followed by 238 h at 40 °C.

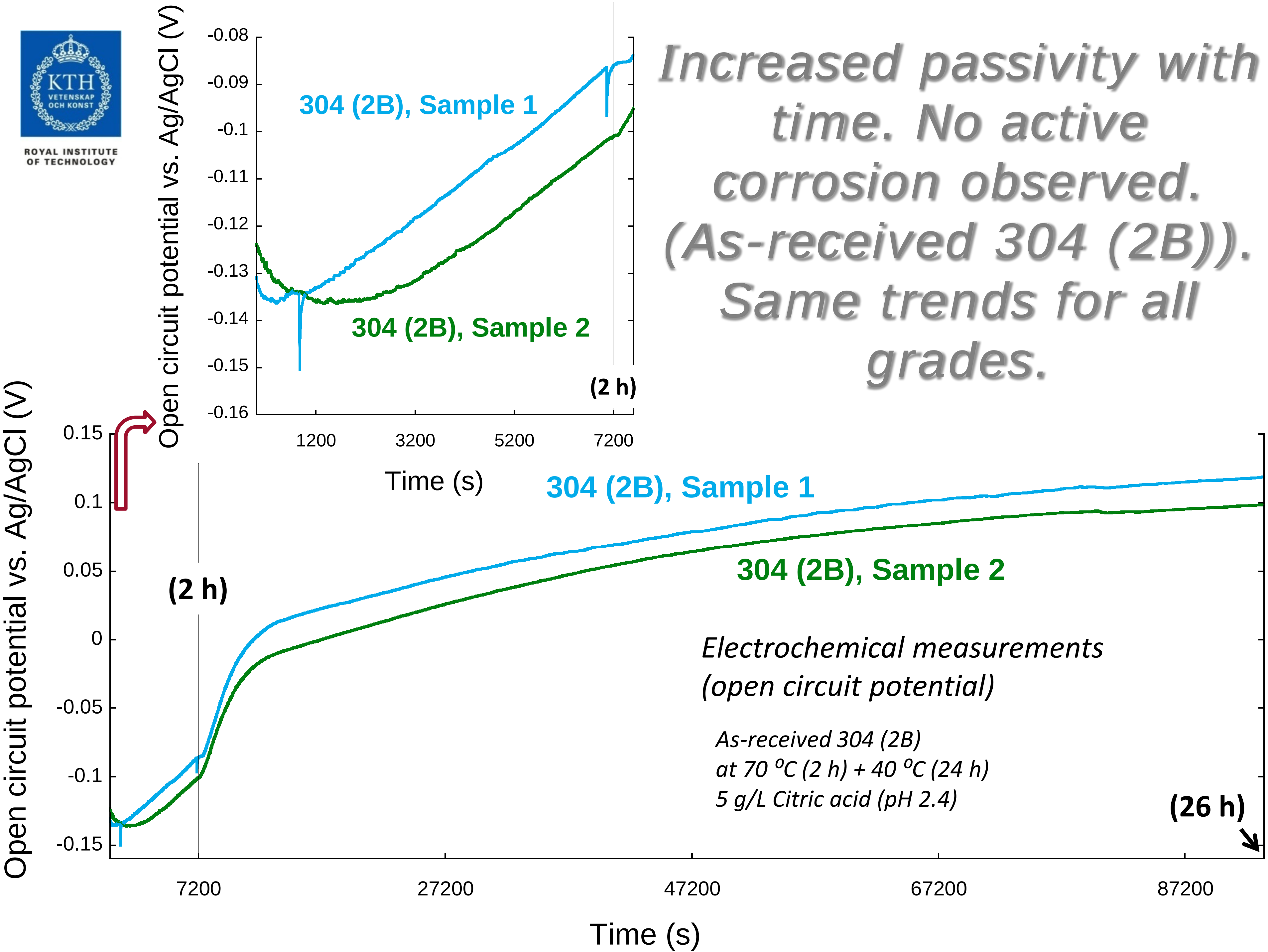
Fe and Mn preferentially released from all grades into citric acid. No correlation with relative surface oxide or bulk nominal composition.



As-received surfaces

Exposure in citric acid (pH 2.4) for 10 days (2 h at 70 °C followed by 238 h at 40 °C).

Increased passivity with time. No active corrosion observed. (As-received 304 (2B)). Same trends for all grades.



Electrochemical measurements (open circuit potential)

As-received 304 (2B)
at 70 ^oC (2 h) + 40 ^oC (24 h)
5 g/L Citric acid (pH 2.4)

ROYAL INSTITUTE
OF TECHNOLOGY

Stripping voltammetry measurements: No Cr(VI) detected in artificial tap water (pH 7.5) or citric acid solutions (pH 2.4 and 4.5) after exposure of as-received 201 and 304 up to 10 days (70/40 °C)

Limit of determination – 0.1 µg/L

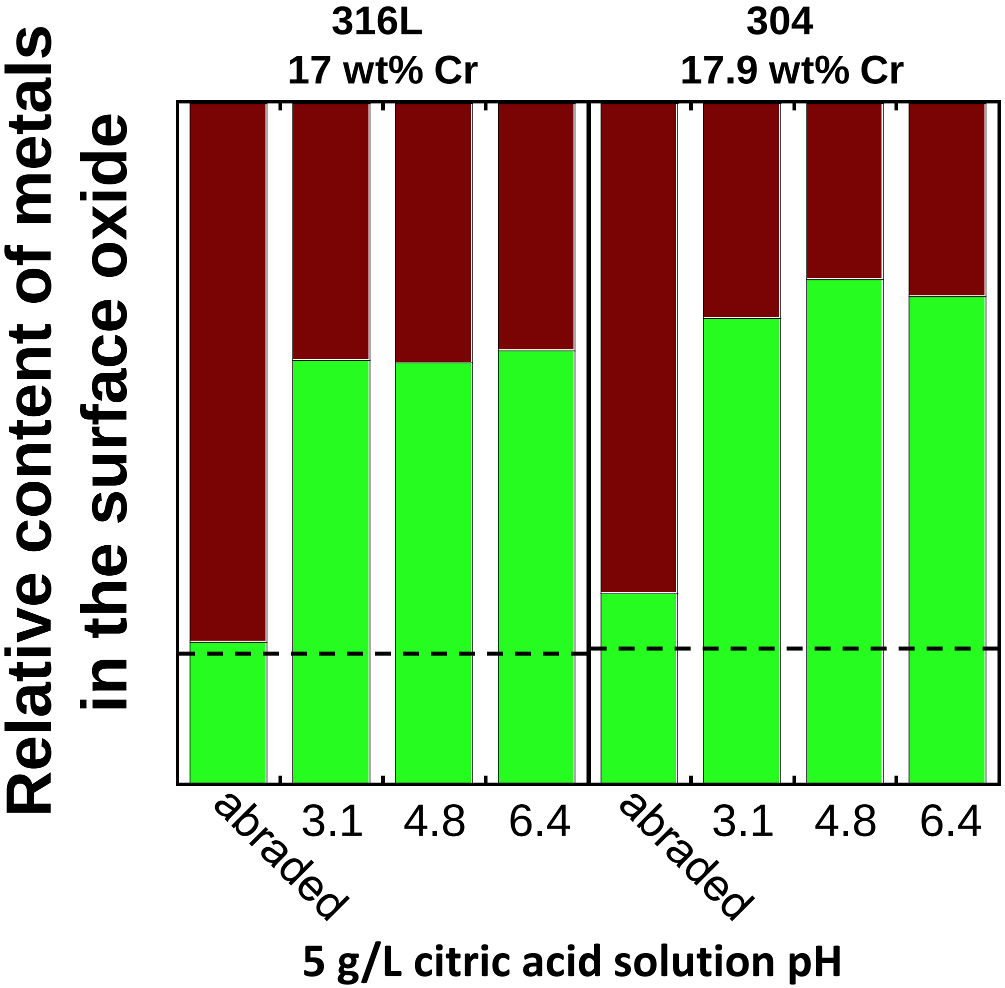
ROYAL INSTITUTE
OF TECHNOLOGY

Effect of pH and citric acid concentration

Cr enrichment in the surface oxide of grades 316L and 304 upon exposure to citric acid solutions of varying pH (3.1 to 6.4).

Surface oxide – XPS

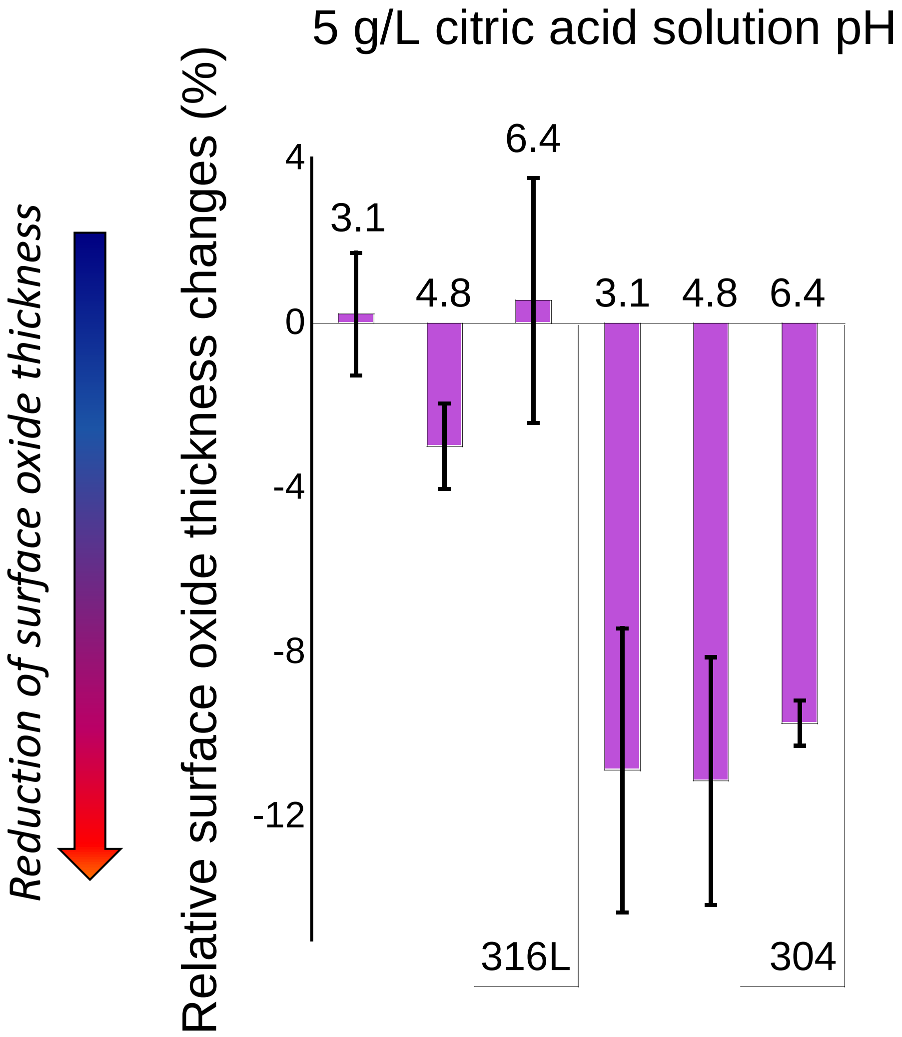
abraded (1200 SiC) and 24 h-aged
70 ^oC (first 2 h) + 40 ^oC (24 h)



Reduction and/or minor changes in surface oxide thickness of grades 316L and 304 after exposure to citric acid solutions of varying pH (3.1 to 6.4)

Surface oxide – XPS

Grades 316L and 304
Abraded (1200 SiC) and 24 h-aged
Citric acid pH 3.1, 4.8, and 6.4
70 ^{o}C (first 2 h) + 40 ^{o}C (24 h)



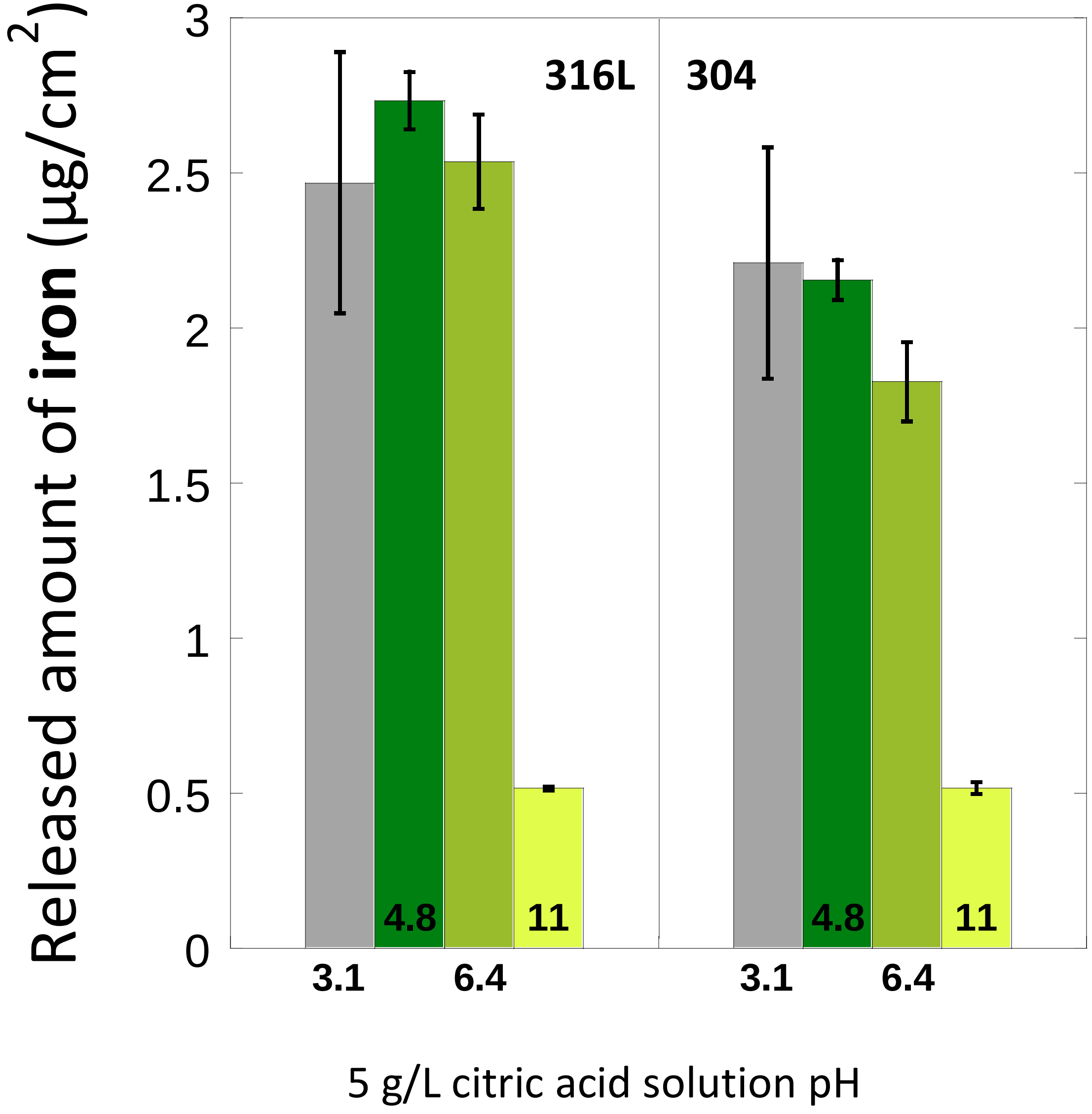
Both pH and the presence of citric acid govern the Fe release.

ROYAL INSTITUTE
OF TECHNOLOGY

Metal release-AAS

Grades 316L and 304
Abraded (1200 SiC) and 24 h-aged
Citric acid pH 3.1, 4.8, and 6.4
70 ^{o}C (first 2 h) + 40 ^{o}C (24 h)

- 🟩 5 g/L citric acid pH 3.1 (70/40 ^{o}C)
- 🟩 5 g/L citric acid pH 4.8 (70/40 ^{o}C)
- 🟨 5 g/L citric acid pH 6.4 (70/40 ^{o}C)
- 🟨 5 g/L citric acid pH 11 (70/40 ^{o}C)



ROYAL INSTITUTE OF TECHNOLOGY

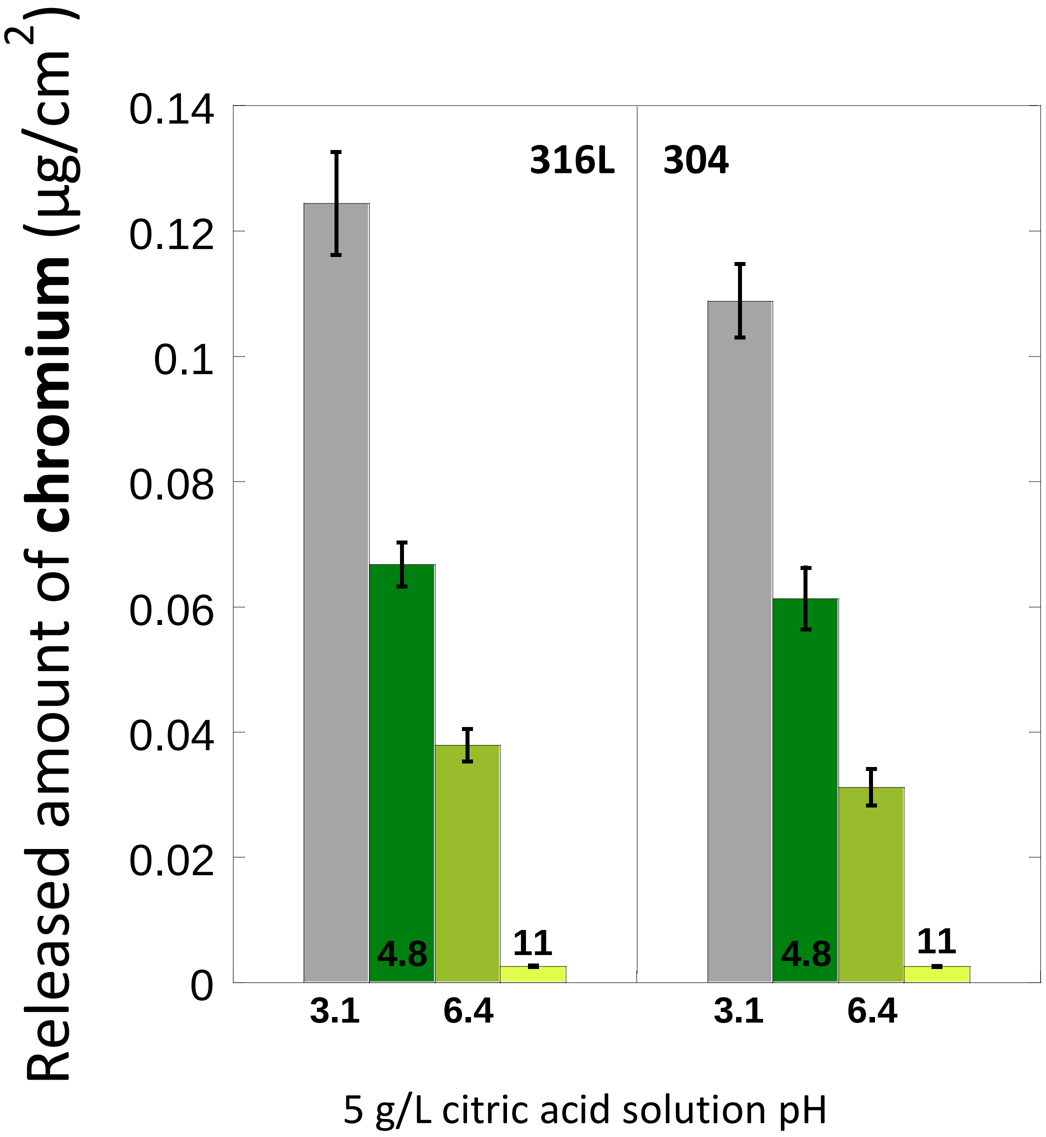
Both pH and the presence of citric acid govern the Cr release, pH is more important.

Metal release-AAS

Grade	304	316L
Cr (wt%)	17.9	17.0

Grades 316L and 304
Abraded (1200 SiC) and 24 h-aged
Citric acid pH 3.1, 4.8, and 6.4
70 ^{o}C (first 2 h) + 40 ^{o}C (24 h)

- 🟩 5 g/L citric acid pH 3.1 (70/40 ^{o}C)
- 🟩 5 g/L citric acid pH 4.8 (70/40 ^{o}C)
- 🟨 5 g/L citric acid pH 6.4 (70/40 ^{o}C)
- 🟨 5 g/L citric acid pH 11 (70/40 ^{o}C)



Both pH and the presence of citric acid govern the Mn release.

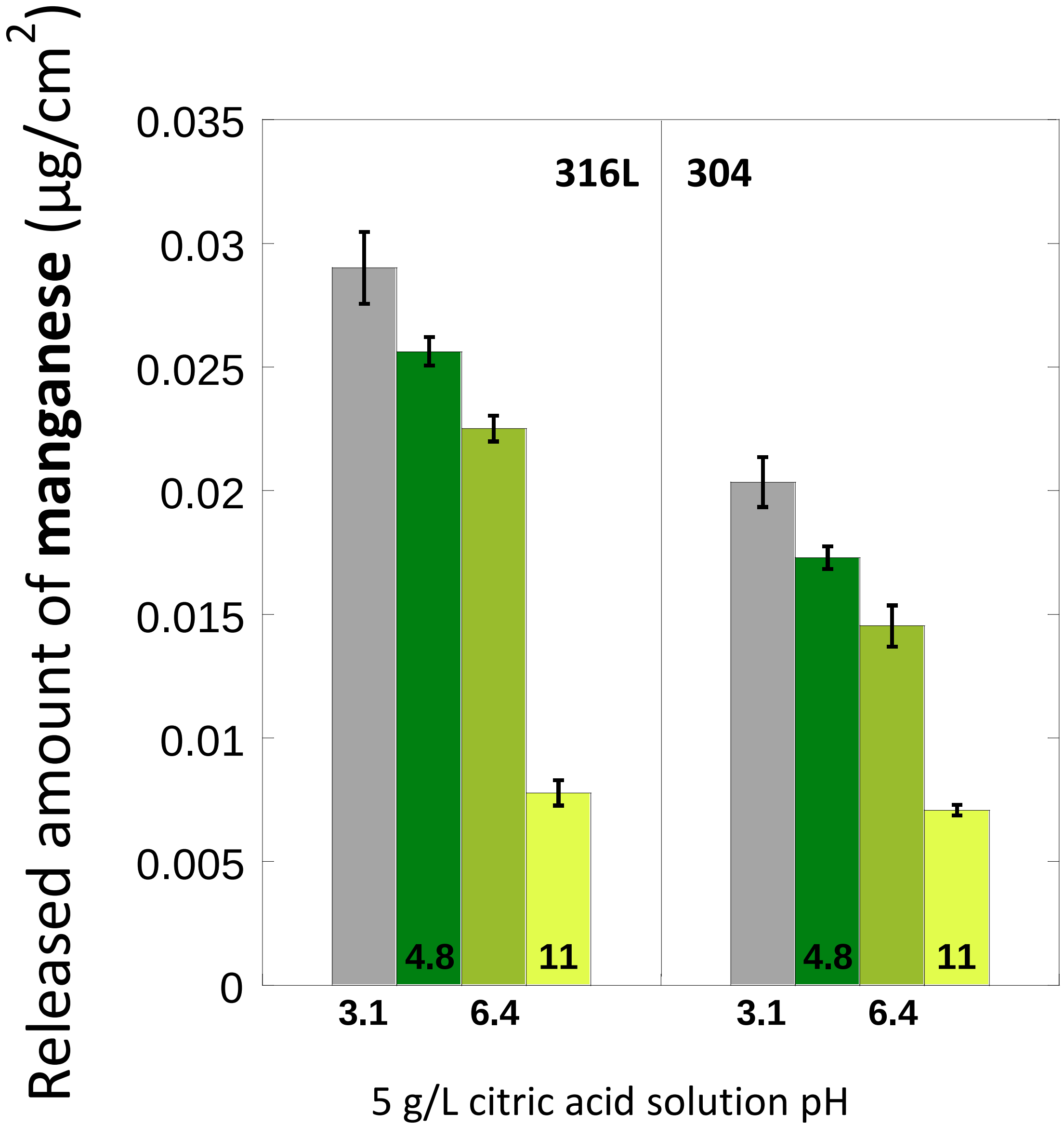
ROYAL INSTITUTE OF TECHNOLOGY

Metal release-AAS

Grade	304	316L
Mn (wt%)	1.2	1.3

Grades 316L and 304
Abraded (1200 SiC) and 24 h-aged
Citric acid pH 3.1, 4.8, and 6.4
70 ^{o}C (first 2 h) + 40 ^{o}C (24 h)

- 🟩 5 g/L citric acid pH 3.1 (70/40 ^{o}C)
- 🟩 5 g/L citric acid pH 4.8 (70/40 ^{o}C)
- 🟨 5 g/L citric acid pH 6.4 (70/40 ^{o}C)
- 🟨 5 g/L citric acid pH 11 (70/40 ^{o}C)



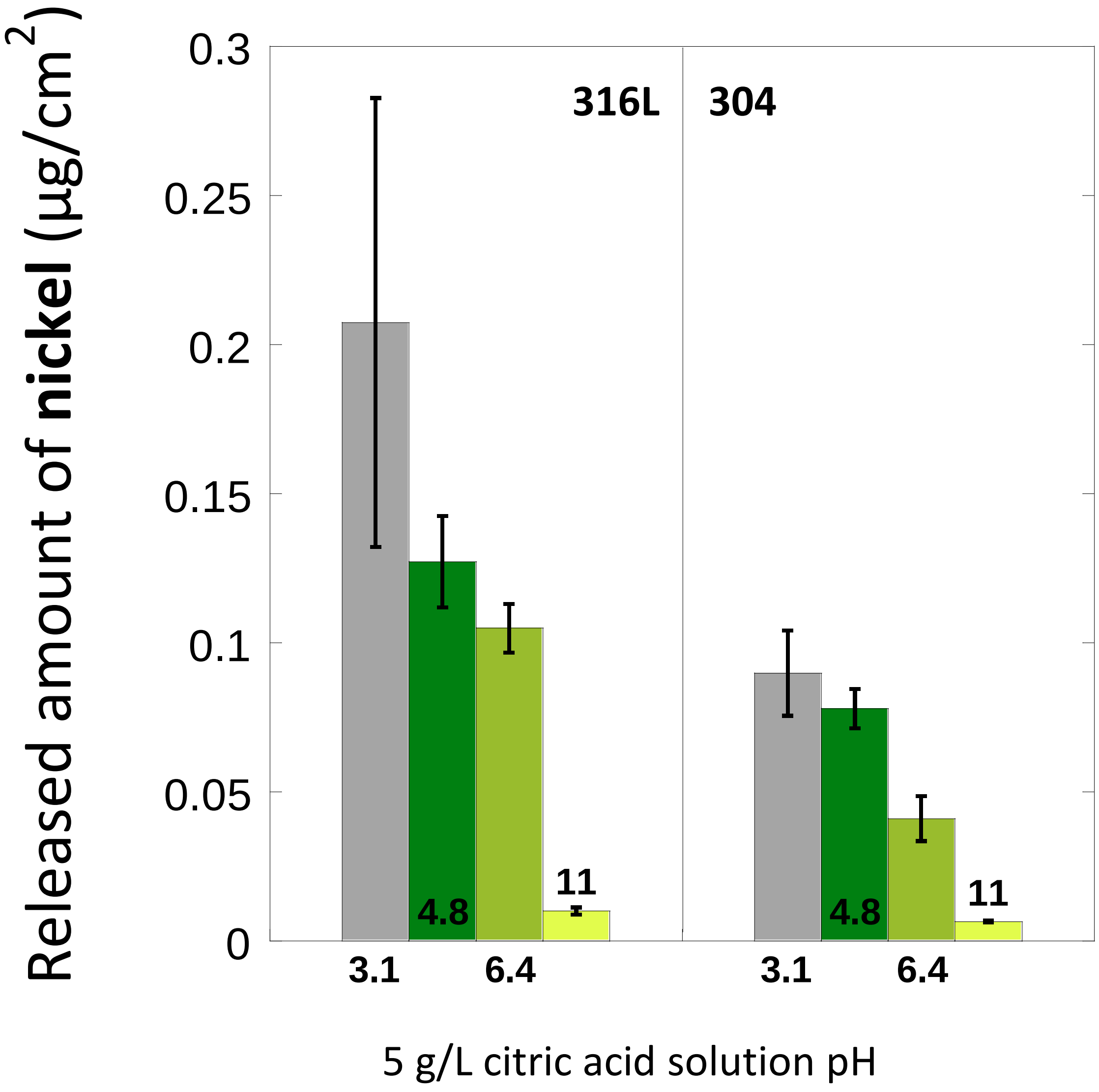
Both pH and the presence of citric acid govern the Ni release.

Metal release-AAS

Grade	304	316L
Ni (wt%)	9.0	10.2

Grades 316L and 304
Abraded (1200 SiC) and 24 h-aged
Citric acid pH 3.1, 4.8, and 6.4
70 °C (first 2 h) + 40 °C (24 h)

- 🟩 5 g/L citric acid pH 3.1 (70/40 °C)
- 🟩 5 g/L citric acid pH 4.8 (70/40 °C)
- 🟨 5 g/L citric acid pH 6.4 (70/40 °C)
- 🟨 5 g/L citric acid pH 11 (70/40 °C)



ROYAL INSTITUTE
OF TECHNOLOGY

Citric acid contributes largely to the extent of released metals from grade 304, independent of solution pH.

pH 3.1, 4.8, 6.4, 11

Abraded and aged surfaces (304)

$$Fe_{\text{citric acid}} \approx (200\text{-}800) \times Fe_{\text{tap water}}$$

$$Cr_{\text{citric acid}} \approx (15\text{-}240) \times Cr_{\text{tap water}}$$

$$Ni_{\text{citric acid}} \approx (0.5\text{-}17) \times Ni_{\text{tap water}}$$

$$Mn_{\text{citric acid}} \approx (3\text{-}8) \times Mn_{\text{tap water}}$$

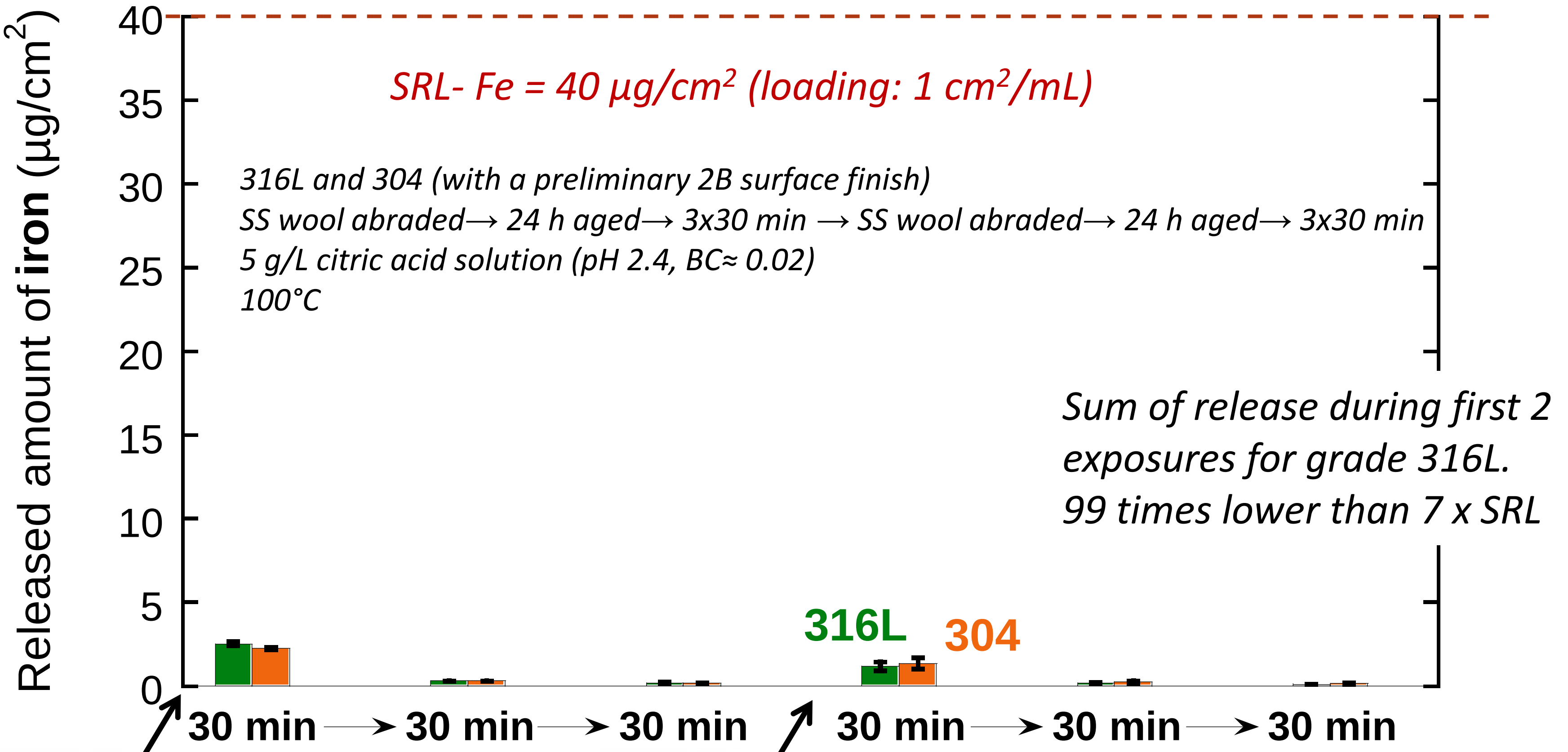
pH 7.5

As-received (2B), edge-ground, and aged surfaces (304)

ROYAL INSTITUTE
OF TECHNOLOGY

Correlation between repeated use and metal release behavior of abraded (stainless steel wool) grades 304 and 316L.

More Fe released during the 1st 30 min exposure at 100 °C, and after SS wool abrasion compared with the 2nd and 3rd exposure for grades 316L and 304 in citric acid (pH 2.4).

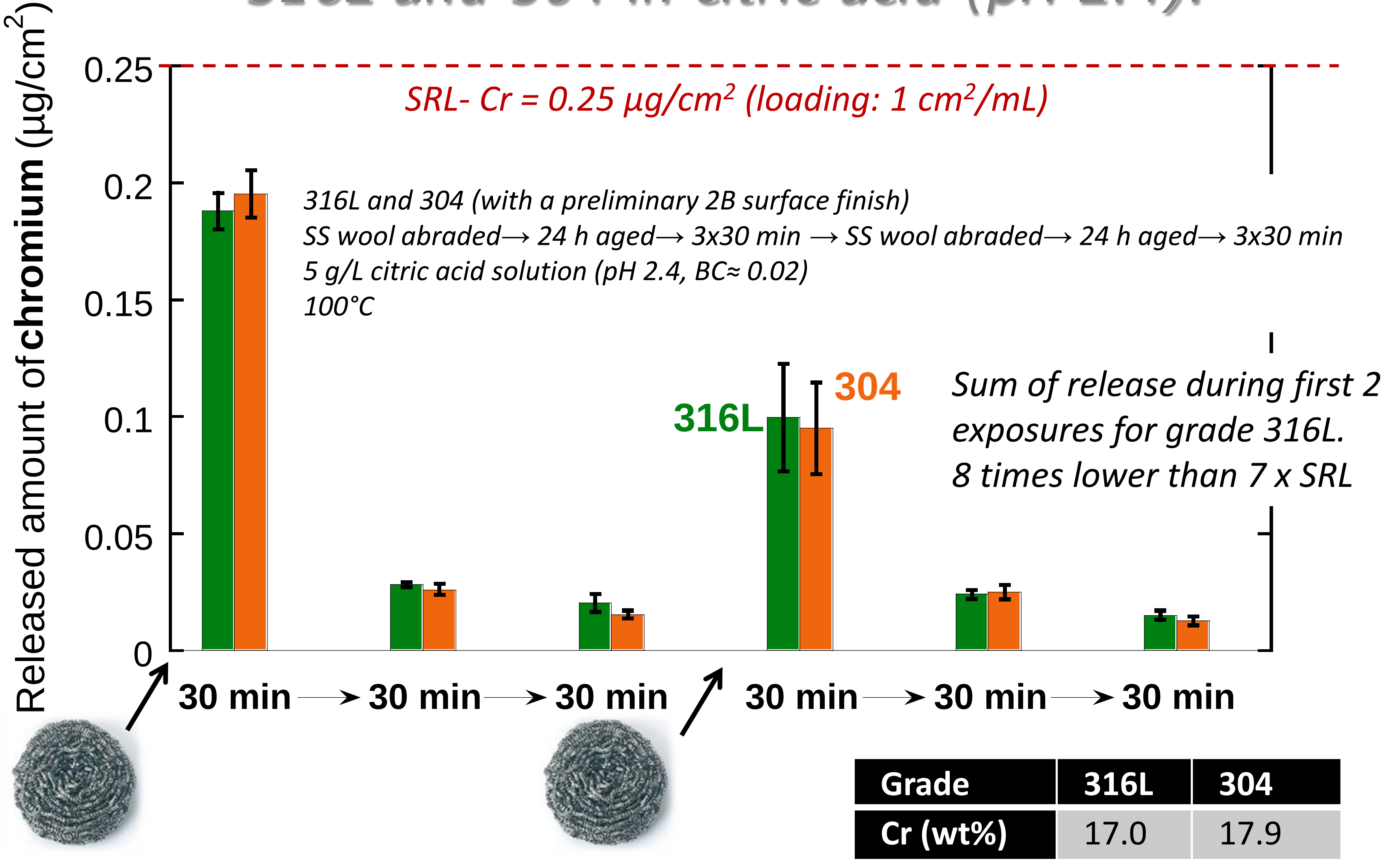


SRL- Fe = 40 µg/cm² (loading: 1 cm²/mL)

316L and 304 (with a preliminary 2B surface finish)
SS wool abraded→ 24 h aged→ 3x30 min → SS wool abraded→ 24 h aged→ 3x30 min
5 g/L citric acid solution (pH 2.4, BC≈ 0.02)
100°C

Sum of release during first 2 exposures for grade 316L. 99 times lower than 7 x SRL

More Cr released during the 1st exposure cycle at 100 °C, and after SS wool abrasion compared with the 2nd and 3rd exposure for grades 316L and 304 in citric acid (pH 2.4).



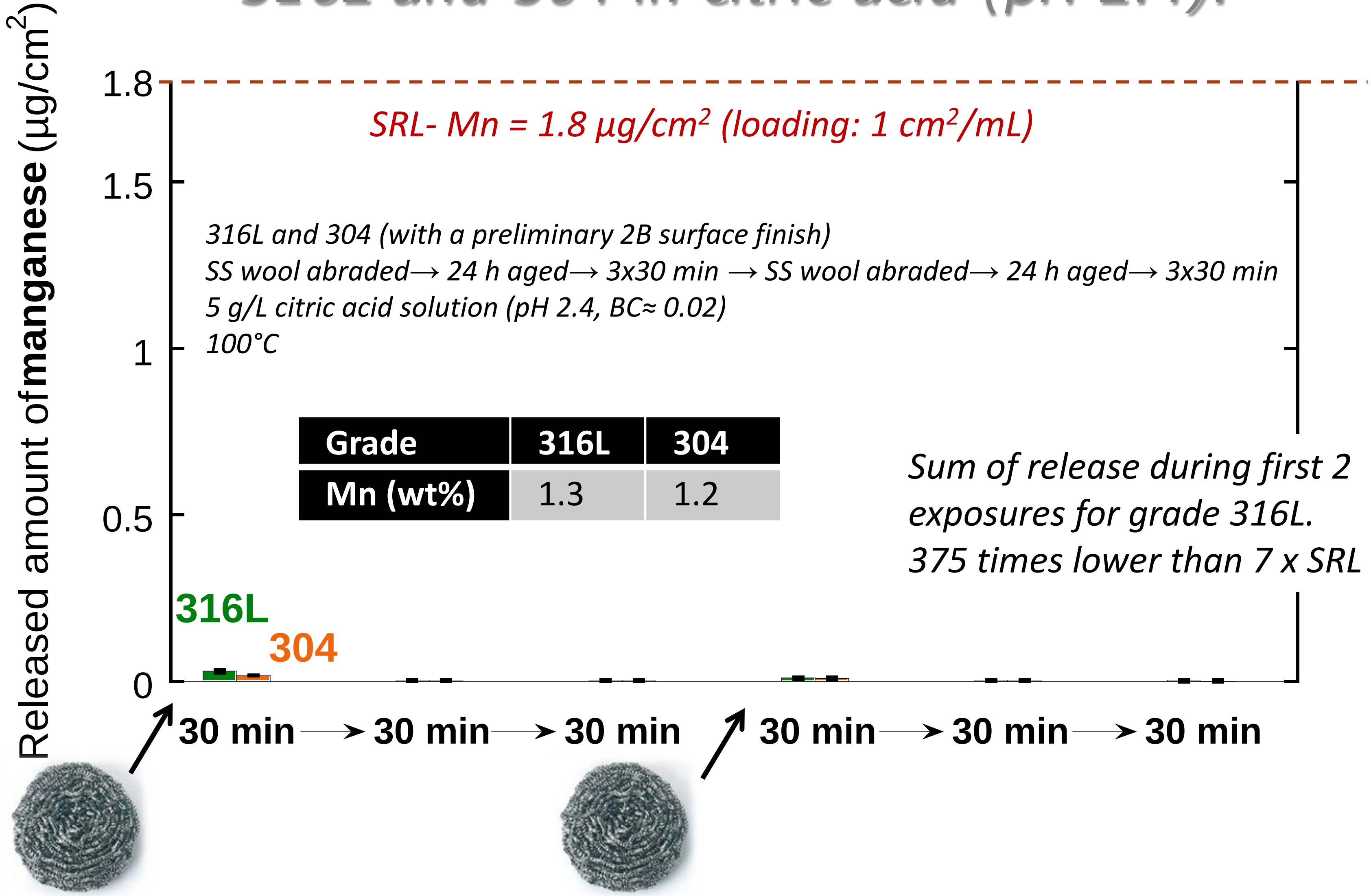
SRL- Cr = 0.25 µg/cm^2 (loading: 1 cm^2/mL)

316L and 304 (with a preliminary 2B surface finish)
SS wool abraded→ 24 h aged→ 3x30 min → SS wool abraded→ 24 h aged→ 3x30 min
5 g/L citric acid solution (pH 2.4, BC≈ 0.02)
100°C

Sum of release during first 2 exposures for grade 316L. 8 times lower than 7 x SRL

Grade	316L	304
Cr (wt%)	17.0	17.9

More Mn released during the 1st exposure cycle at 100 °C, and after SS wool abrasion compared with the 2nd and 3rd exposure for grades 316L and 304 in citric acid (pH 2.4).



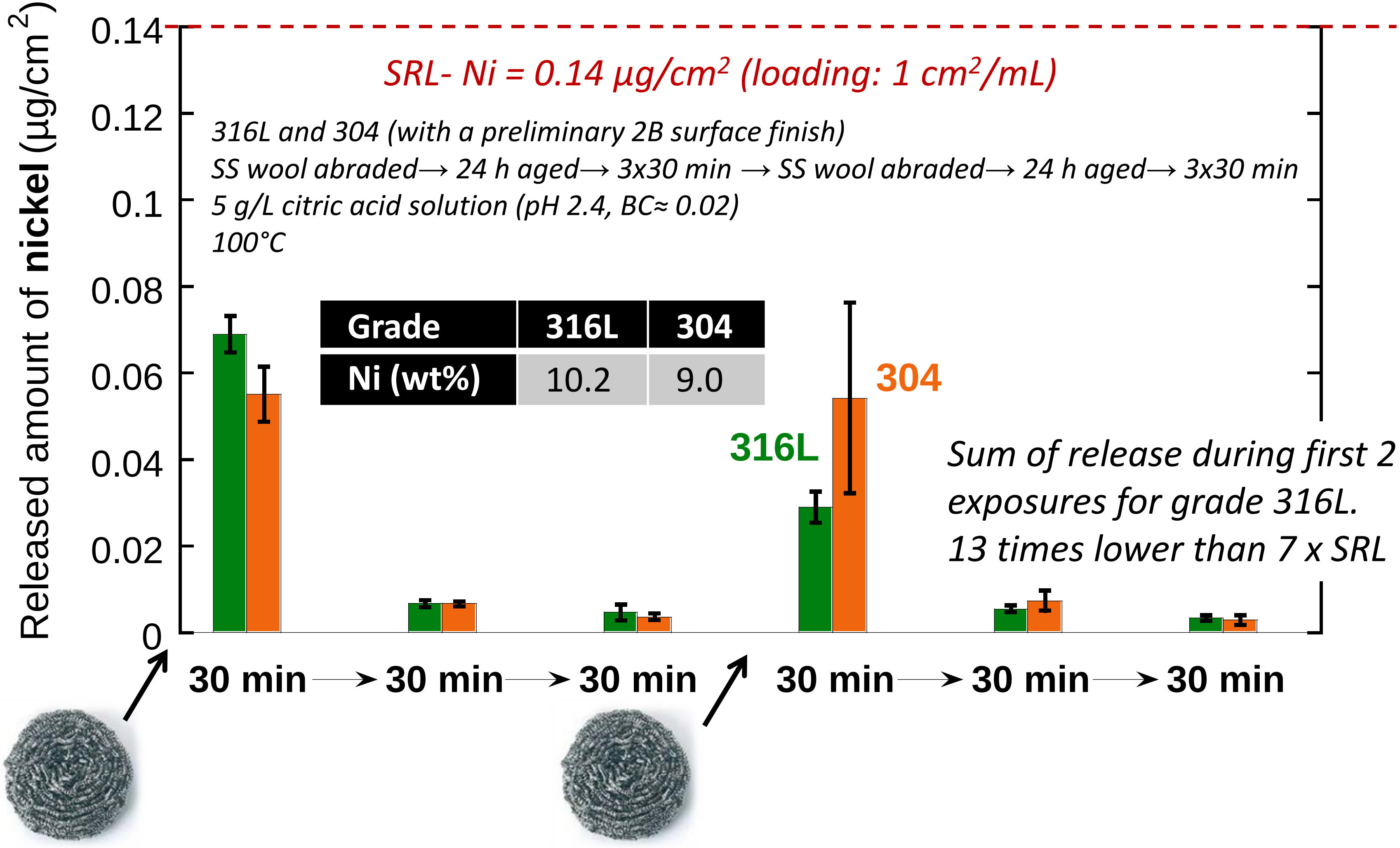
SRL- Mn = 1.8 µg/cm^2 (loading: 1 cm^2/mL)

316L and 304 (with a preliminary 2B surface finish)
SS wool abraded→ 24 h aged→ 3x30 min → SS wool abraded→ 24 h aged→ 3x30 min
5 g/L citric acid solution (pH 2.4, BC≈ 0.02)
100°C

Grade	316L	304
Mn (wt%)	1.3	1.2

Sum of release during first 2 exposures for grade 316L. 375 times lower than 7 x SRL

More Ni released during the 1st exposure cycle at 100 °C, and after SS wool abrasion compared with the 2nd and 3rd exposure for grades 316L and 304 in citric acid (pH 2.4).



SRL- Ni = 0.14 µg/cm² (loading: 1 cm²/mL)

316L and 304 (with a preliminary 2B surface finish)
SS wool abraded→ 24 h aged→ 3x30 min → SS wool abraded→ 24 h aged→ 3x30 min
5 g/L citric acid solution (pH 2.4, BC≈ 0.02)
100°C

Grade	316L	304
Ni (wt%)	10.2	9.0

Sum of release during first 2 exposures for grade 316L. 13 times lower than 7 x SRL

ROYAL INSTITUTE
OF TECHNOLOGY

Investigation of different surface finishes (No. 4 and Scotch-Brite) for the same grade (304 and 316L)

Investigated grades + synthetic fluids + exposure conditions.

Investigated grades of stainless steels (based on supplier information)

Name (in this report)	UNS (ASTM A 240)	Surface finish	Cr wt%	Mn wt%	Ni wt%	Mo wt%	Cu wt%	N wt%	C wt%
304	S30400	2B	17.9	1.2	9.0	0.4	0.4	0.04	0.04
304	S30400	Sc.-Br. (2J)	using a Scotch-Brite brush						
304	S30400	No. 4 (2G)	polishing with a 320 grit grinding belt						
316L	S31603	2B	17	1.3	10.2	2	0.5	0.05	0.02
316L	S31603	Sc.-Br. (2J)	using a Scotch-Brite brush						
316L	S31603	No. 4 (2G)	polishing with a 220 grit grinding belt						

As-received 304 (SB, N4, and 2B)
As-received 316L (SB, N4, and 2B)

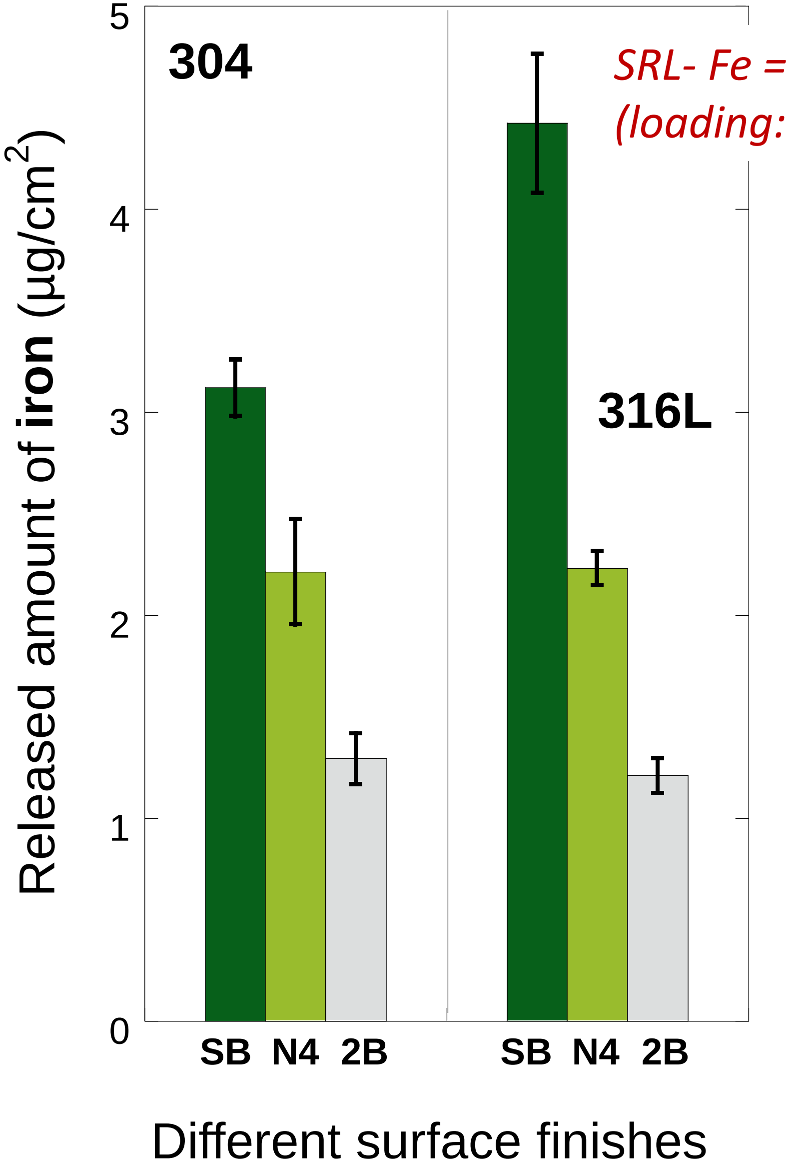
Based on the CoE protocol:
Citric acid pH 2.4
70 ^{o}C (first 2 h) + 40 ^{o}C (24 h)

**loading of this study (0.5 cm^2/mL), since only one of the sample surfaces was finished, the other side was blocked using a metal-free lacquer.*

The release of Fe from grades 316L and 304 reduced according to: Scotch-Brite (SB) > N4 > 2B.

ROYAL INSTITUTE
OF TECHNOLOGY

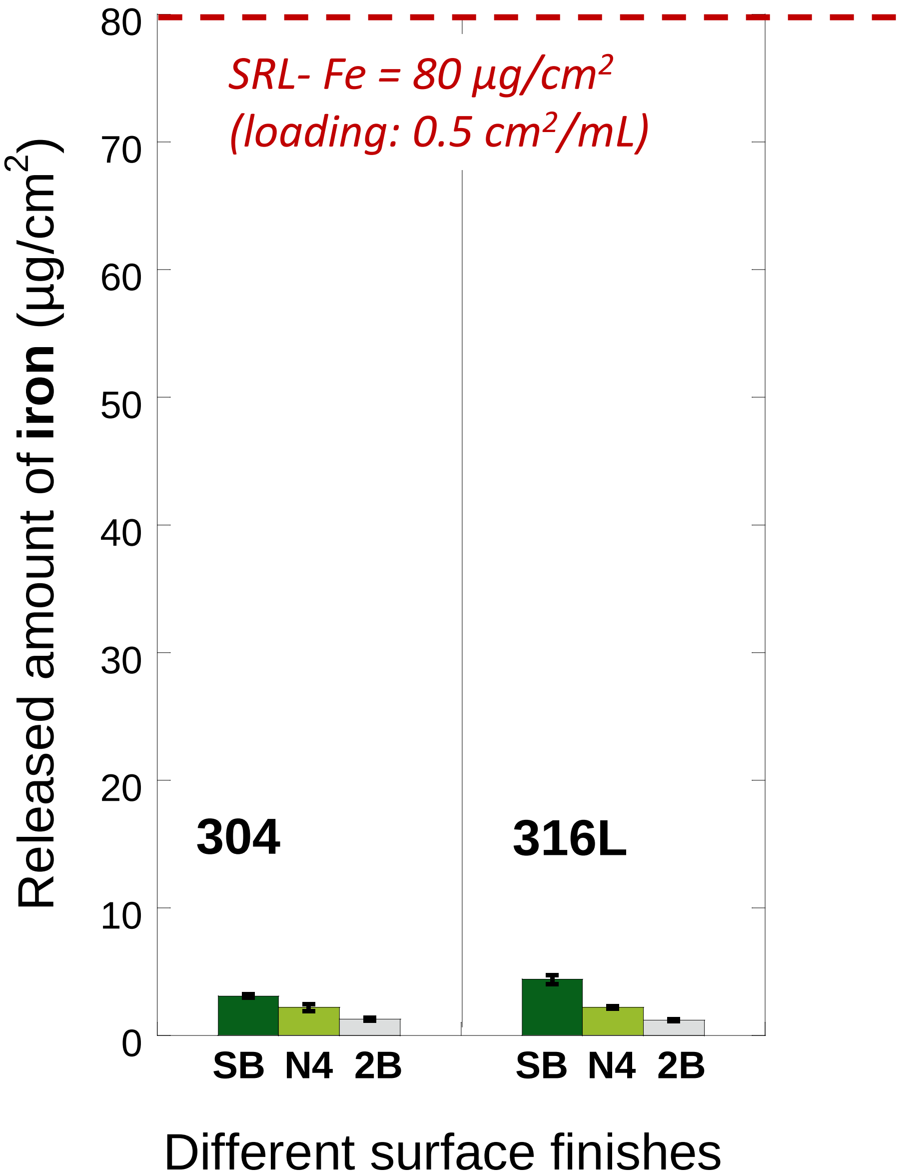
Metal release-AAS



SRL- Fe = 80 µg/cm^2
(loading: 0.5 cm^2/mL)

The release of Fe from grades 316L and 304 reduced according to: Scotch-Brite (SB) > N4 > 2B.

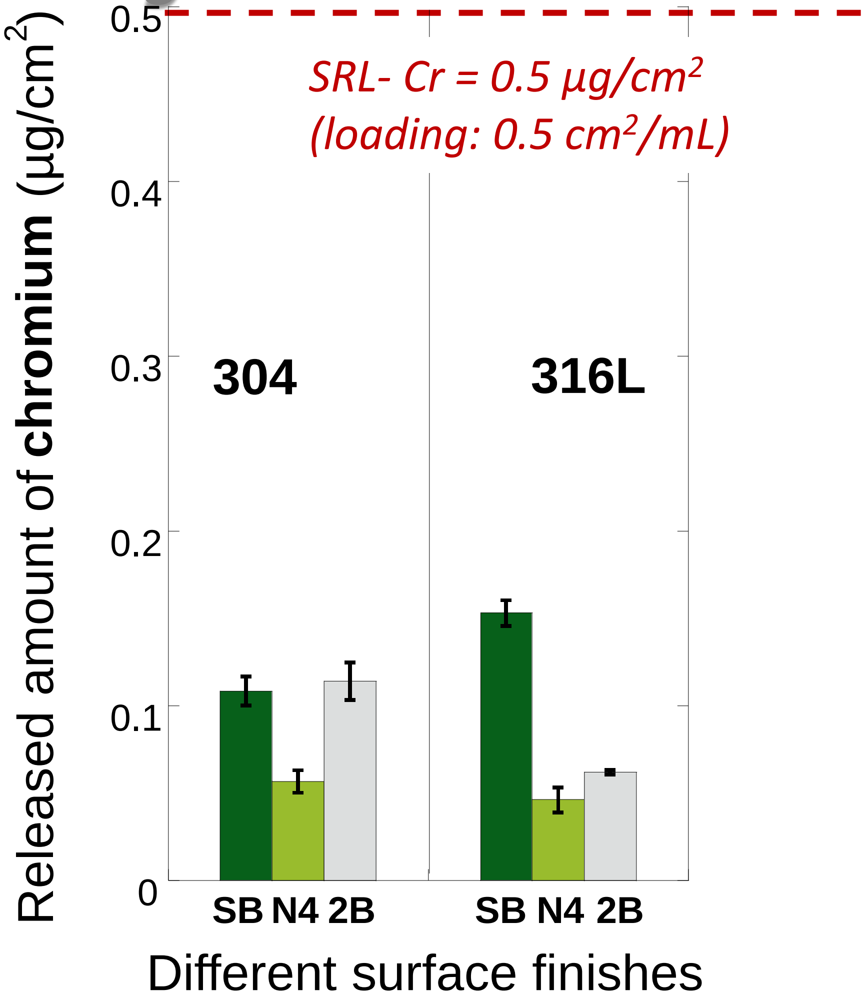
Metal release-AAS



SRL- Fe = 80 µg/cm^2
(loading: 0.5 cm^2/mL)

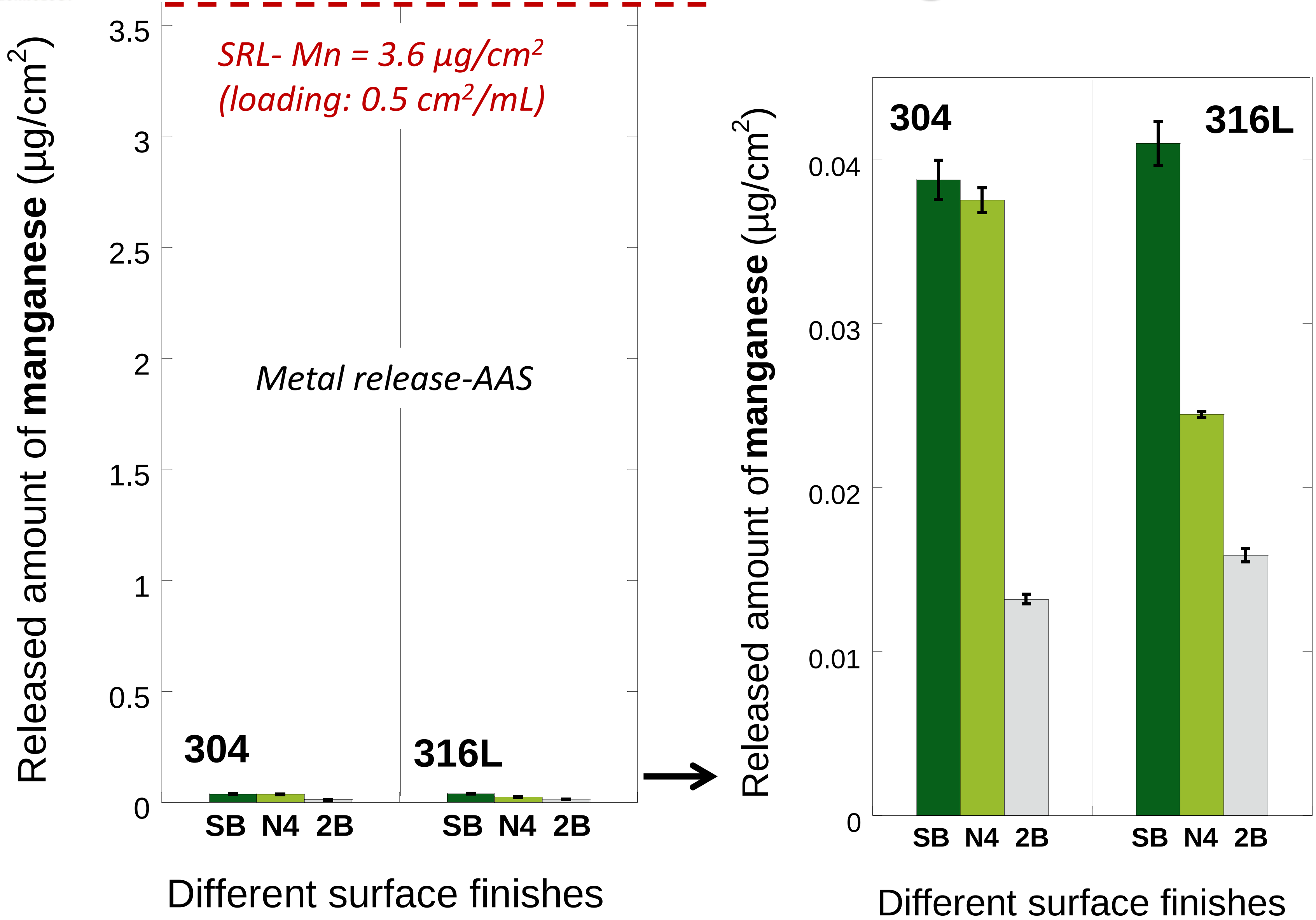
The release of Cr from grade 316L reduced according to: Scotch-Brite (SB) > 2B > N4. No difference between the released amount of Cr from SB and 2B surface finishes for grade 304.

Metal release-AAS



SRL- Cr = 0.5 µg/cm²
(loading: 0.5 cm²/mL)

The release of Mn reduced according to: SB > N4 > 2B, for grade 316L; and SB ≈ N4 > 2B for grade 304.

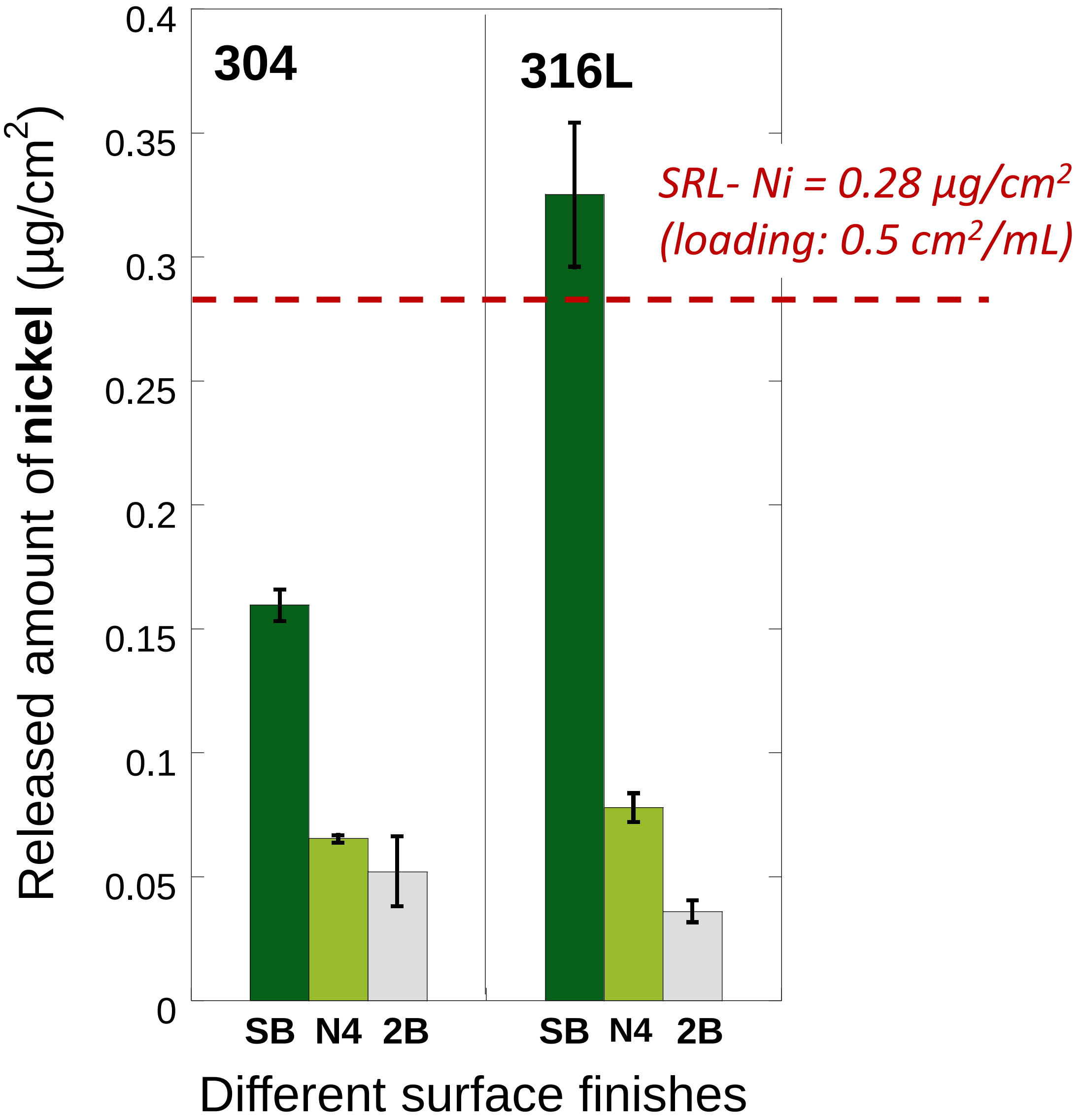


SRL- Mn = 3.6 µg/cm^2
(loading: 0.5 cm^2/mL)

Metal release-AAS

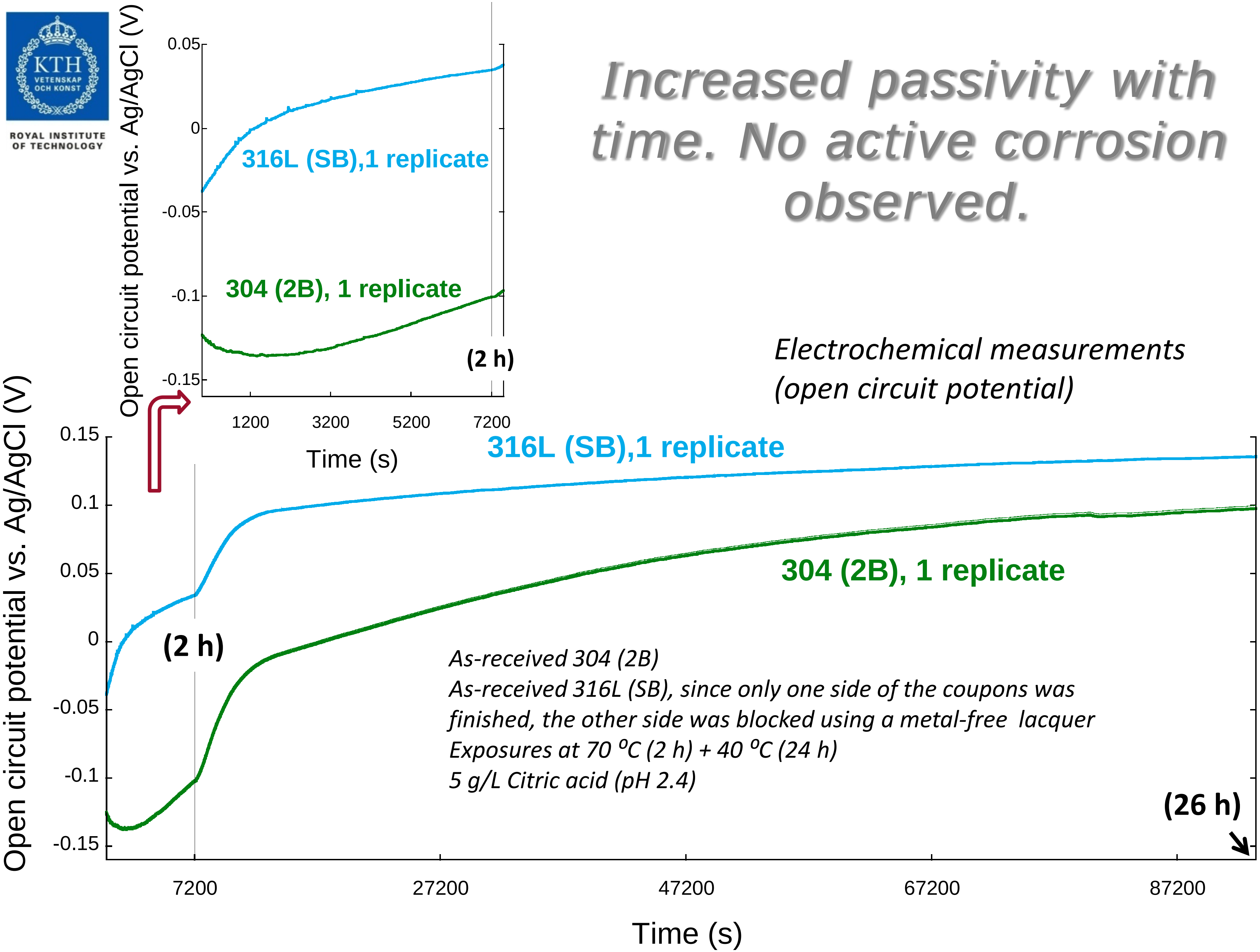
The release of Ni reduced according to SB > N4 > 2B. The release of Ni from SB surface finished grade 316L above the SRL value.

Metal release-AAS



Increased passivity with time. No active corrosion observed.

Electrochemical measurements (open circuit potential)



As-received 304 (2B)
As-received 316L (SB), since only one side of the coupons was finished, the other side was blocked using a metal-free lacquer
Exposures at 70 ^{o}C (2 h) + 40 ^{o}C (24 h)
5 g/L Citric acid (pH 2.4)

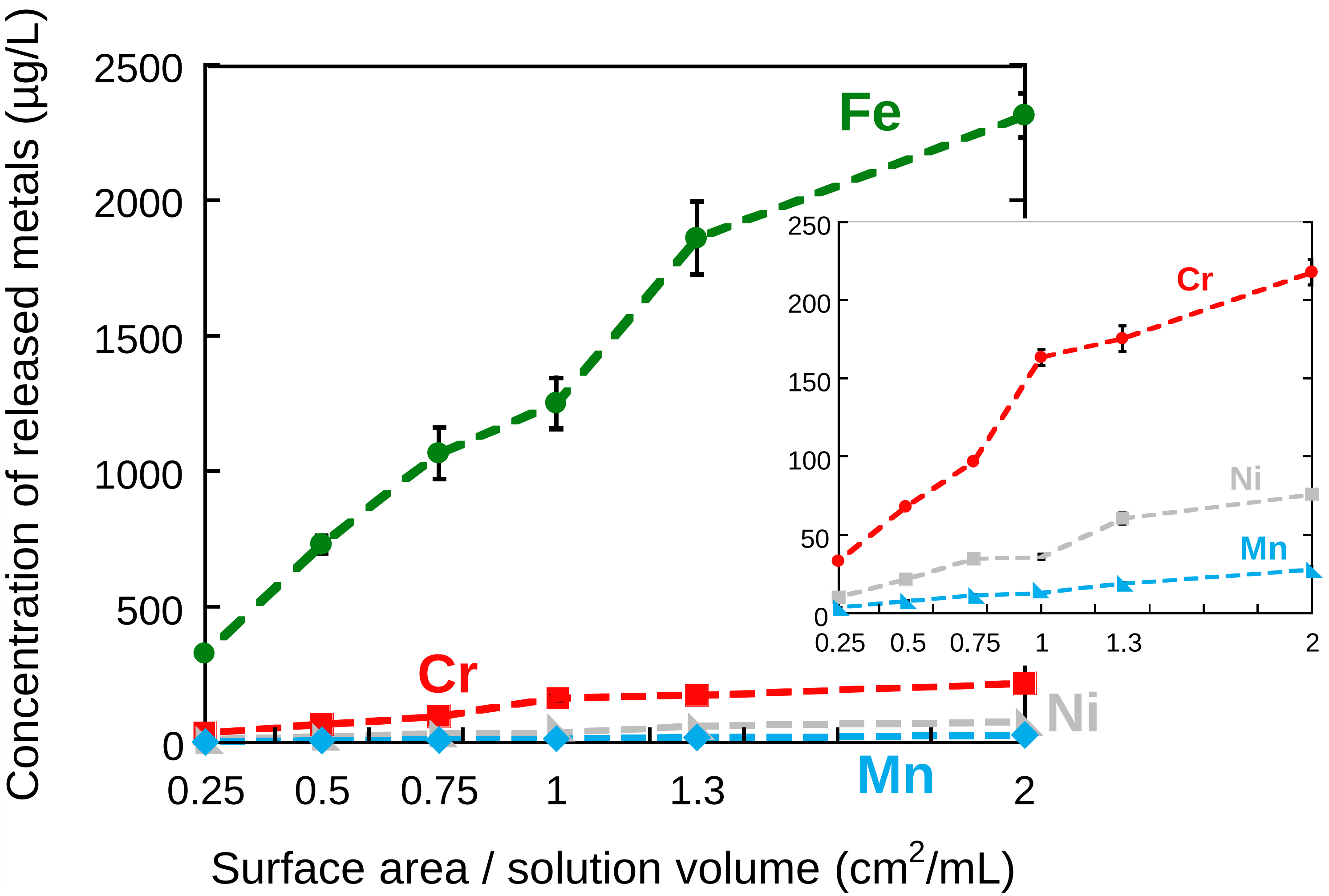
ROYAL INSTITUTE
OF TECHNOLOGY

Illustration of the effect of loading (surface area to solution volume ratio) for as-received 304 (2B)

Higher metal concentrations in solution with higher loading (linear correlation, 0.91≤ R^2 ≤ 0.99).

As-received 304 (2B)
2 h at 70 °C
5 g/L Citric acid (pH 2.4)
Surface to volume ratios:
0.25, 0.5, 0.75, 1, 1.3,
and 2 cm^2/mL

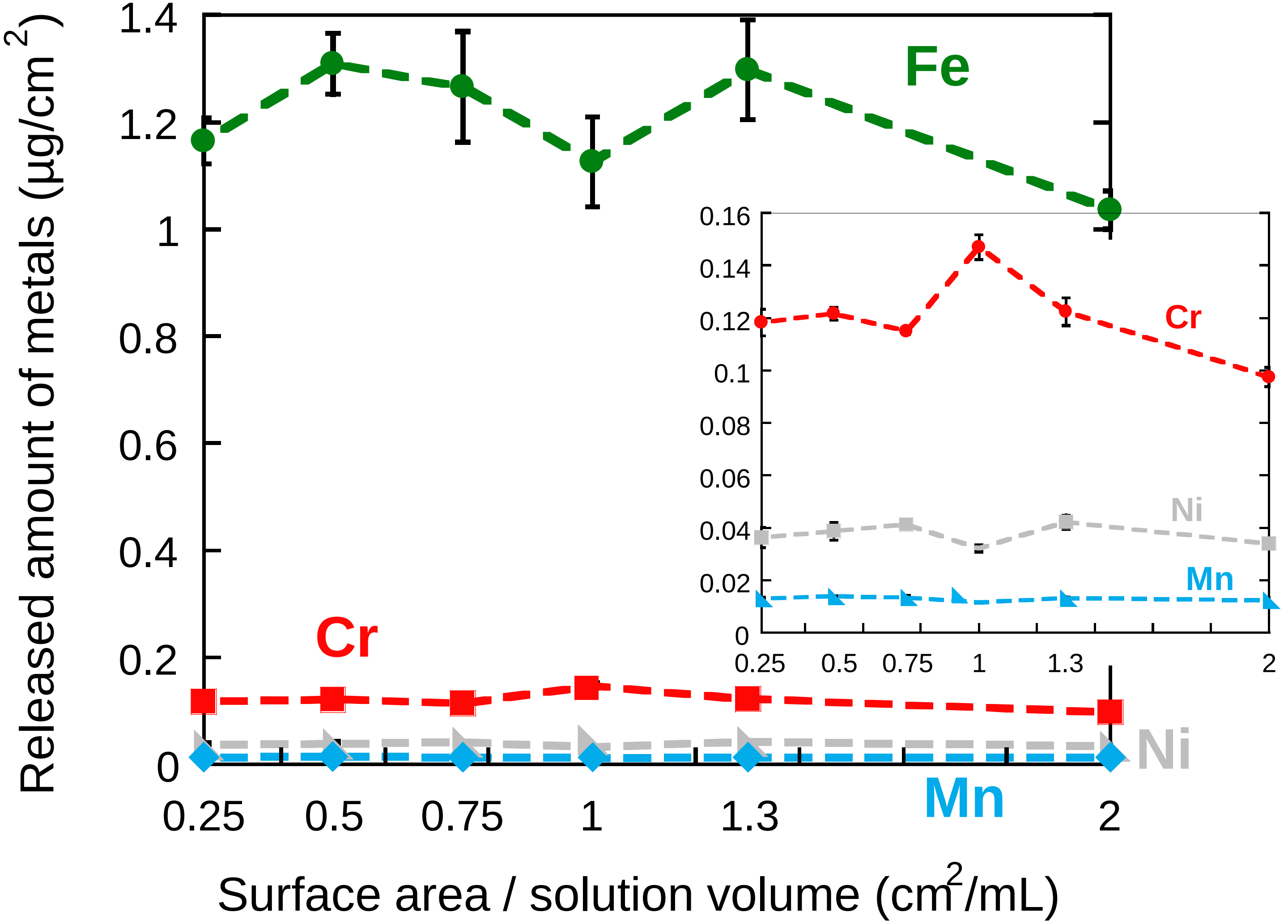
Loading of 1 cm^2/mL



A relatively constant released amount of metals (especially for Ni and Mn) per surface area, independent of exposure condition.

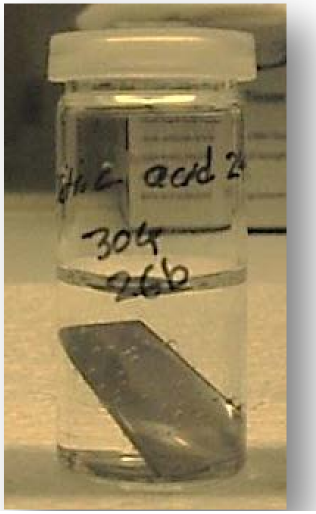
As-received 304 (2B)
2 h at 70 ^{o}C
5 g/L Citric acid (pH 2.4)
Surface to volume ratios:
0.25, 0.5, 0.75, 1, 1.3,
and 2 cm^2/mL

Loading of 1 cm^2/mL

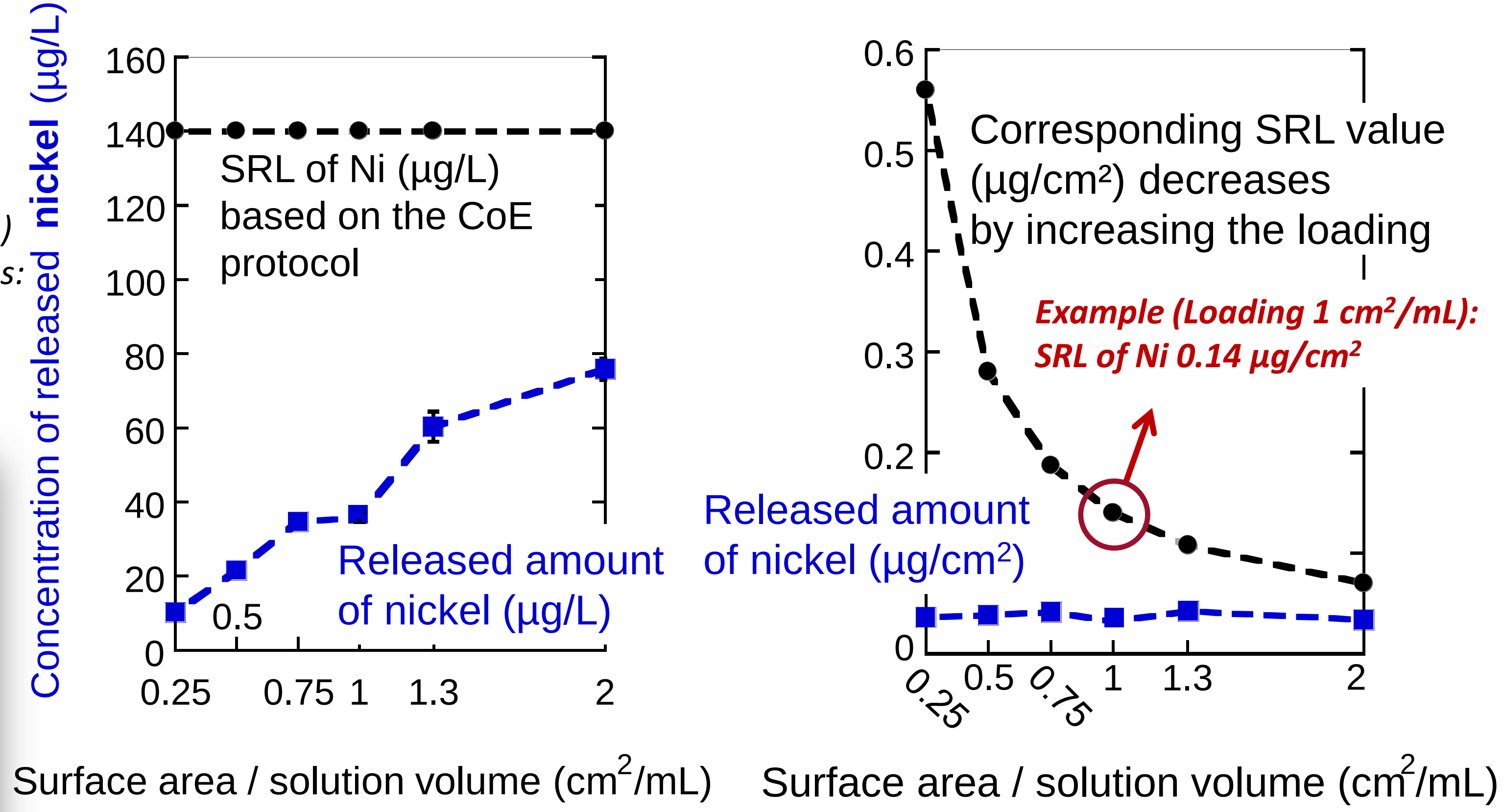


The outcome of a comparison of release data with SRL levels largely depends on the sample loading.

As-received 304 (2B)
2 h at 70 ^{o}C
5 g/L Citric acid (pH 2.4)
Surface to volume ratios:
0.25, 0.5, 0.75, 1, 1.3,
and 2 cm^2/mL



Loading of 1 cm²/mL



SRL of Ni (μg/L) based on the CoE protocol

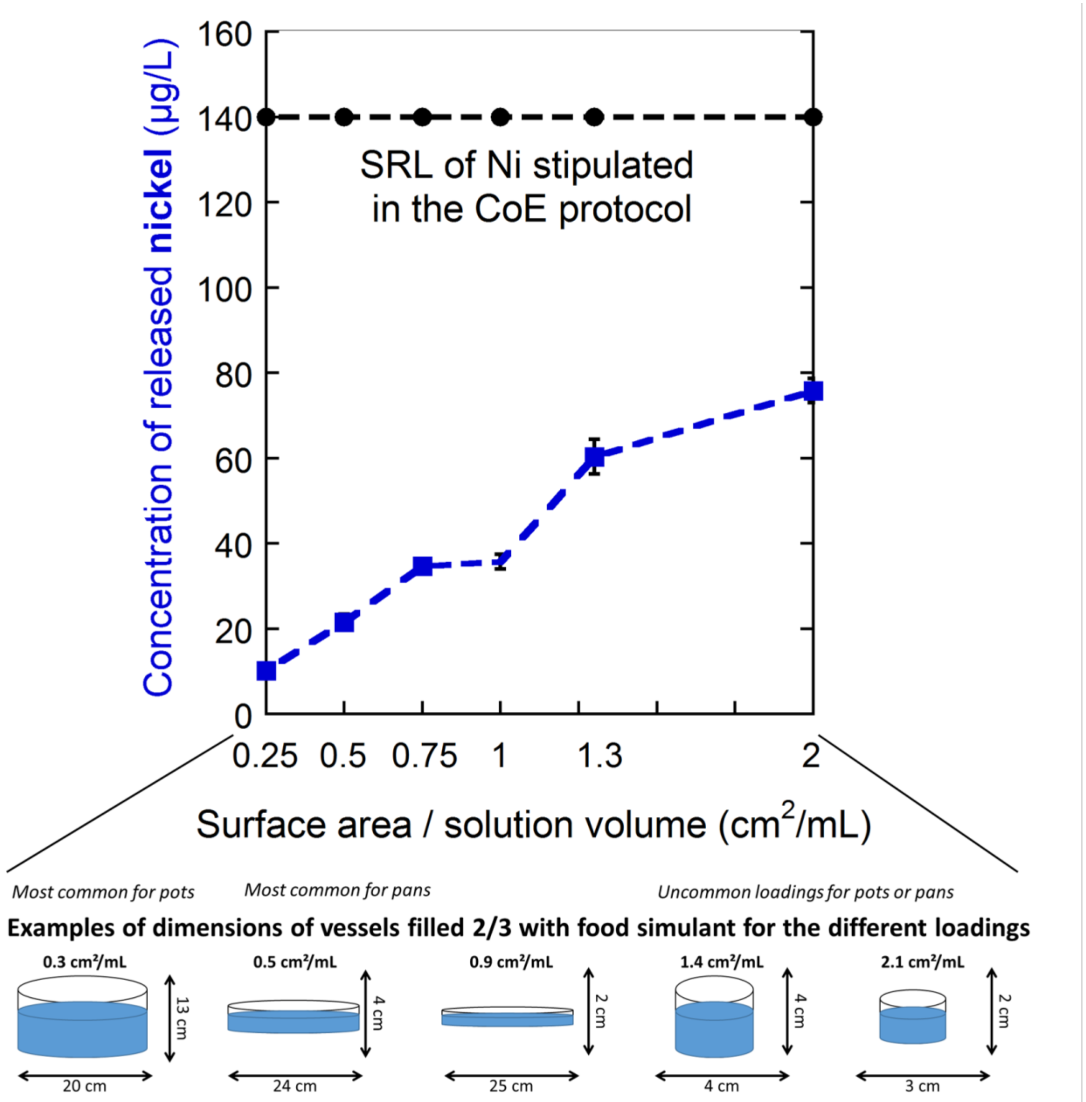
Released amount of nickel (μg/L)

Corresponding SRL value (μg/cm²) decreases by increasing the loading

Example (Loading 1 cm²/mL): SRL of Ni 0.14 μg/cm²

Released amount of nickel (μg/cm²)

Illustration of relevant loadings. 1 cm²/mL (standard loading of this study) is one of the worst cases.



ROYAL INSTITUTE
OF TECHNOLOGY

Degrees of freedom in the CoE protocol.

- An increased temperature results generally in an increased amount of released metals, but can also contribute to improved surface passivity at specific conditions.
- Most metals are released during a short initial period of exposure. Pre-passivation or repeated tests result in reduced amounts of released metals.
- Surface conditions of the stainless steel surface prior to exposure influence the amount of released metal. As a consequence most metals are released during the first two hours of exposure for as-received or abraded surfaces. Repeated exposures, or defined surface preparation conditions in the CoE guideline are recommended.
- An increased surface area to solution volume ratio (loading) results in higher concentrations of released metals. A defined loading in the CoE guideline for general material testing or a defined range of possible loadings for application-specific testing are recommended.

KEY MESSAGES

- The released amounts of metals for all stainless steel grades and test conditions investigated were all below their corresponding release limits (SRLs) stipulated in the CoE protocol.
- Passivation and chromium enrichment of the surface oxide during exposure in citric acid resulted in reduced amounts of released metals with time. Most metals were released from as-received or abraded stainless steel during the very initial exposure period. As a consequence, subsequent exposures resulted in lower released amounts of metals per hour. The released metal fraction from passive stainless steel surfaces is therefore neither proportional to the bulk composition nor to the surface oxide composition.
- Chromium was released in its trivalent form. No hexavalent chromium was released or detected in citric acid for the investigated grades (201 and 304).

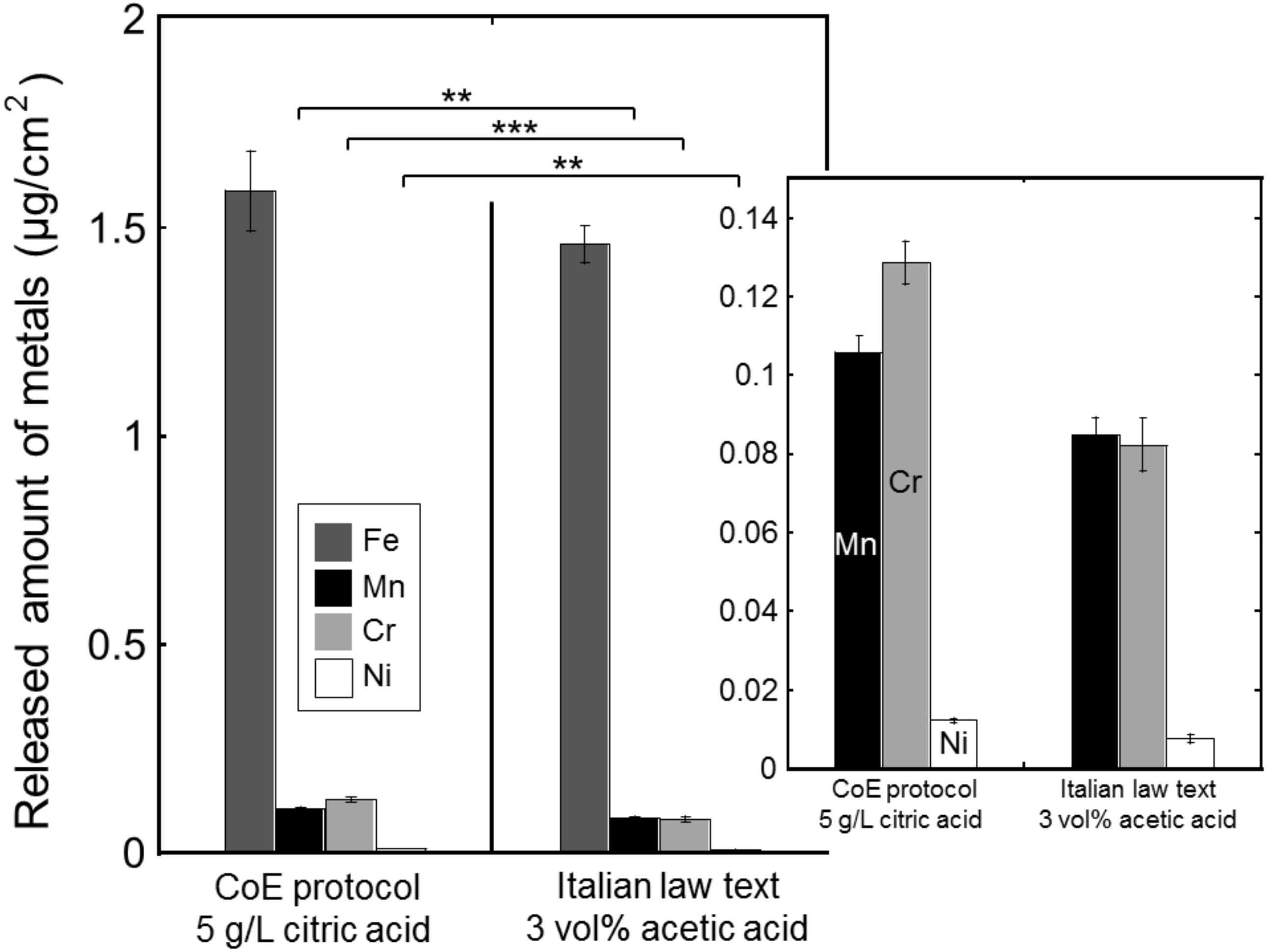
KEY MESSAGES, cont.

- The amounts of released metals were reduced upon repeated use of stainless steel. The surface of the stainless steel passivates fast in citric acid after surface abrasion.
- The surface condition of the stainless steel prior to exposure influences the amount of released metals.
- An increased surface area to solution volume ratio (loading) resulted in higher concentrations of released metals. A loading of 1 cm^2/mL was selected in this study to enable a comparison between different grades and representative for one of the worst cases (e.g. flat pans).

Appendix-1

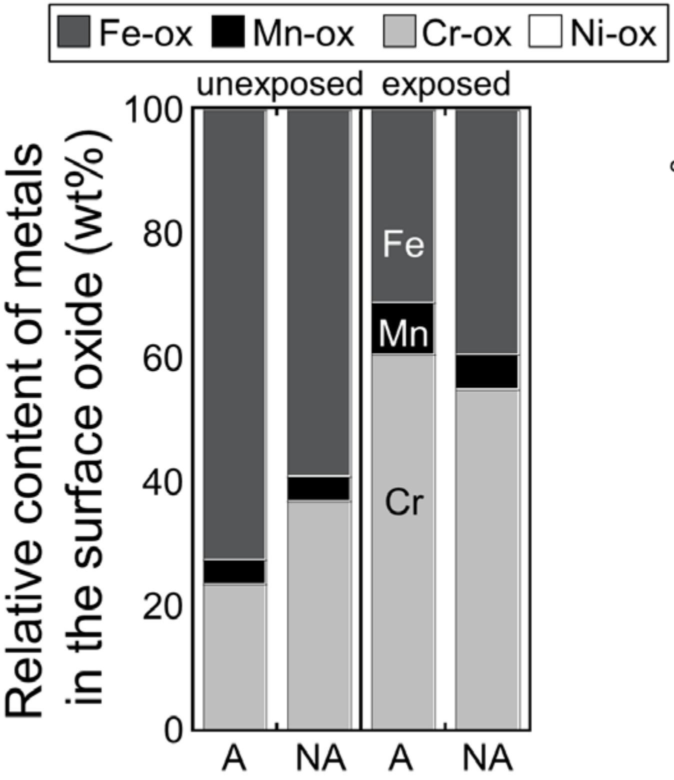
Additional studies on abraded grade 201

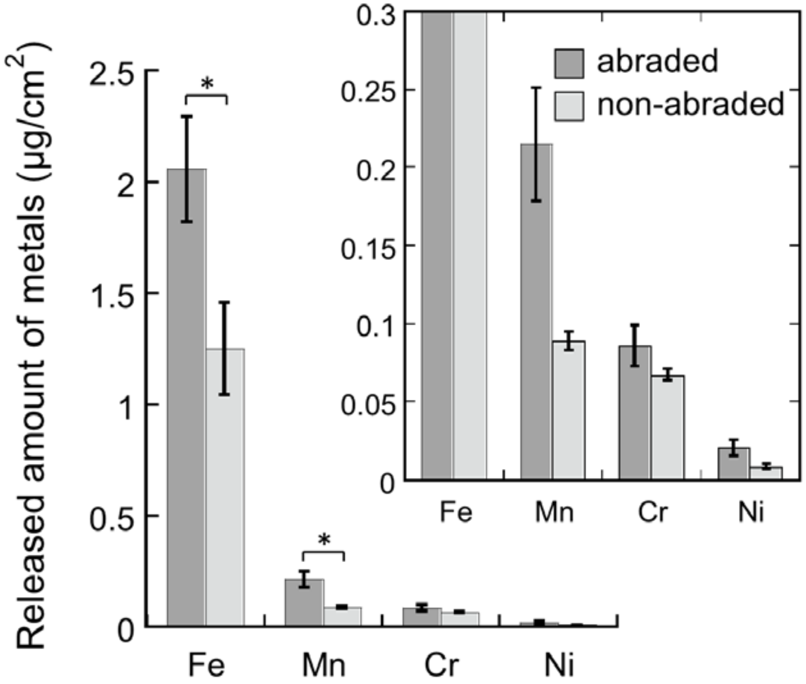
The CoE protocol stipulates more aggressive conditions than the Italian law text from a metal release perspective.



Mazinanian N, Odnevall Wallinder I, Hedberg Y. Comparison of the influence of citric acid and acetic acid as simulant for acidic food on the release of alloy constituents from stainless steel AISI 201, J Food Eng 2015: **145**: 51-63.

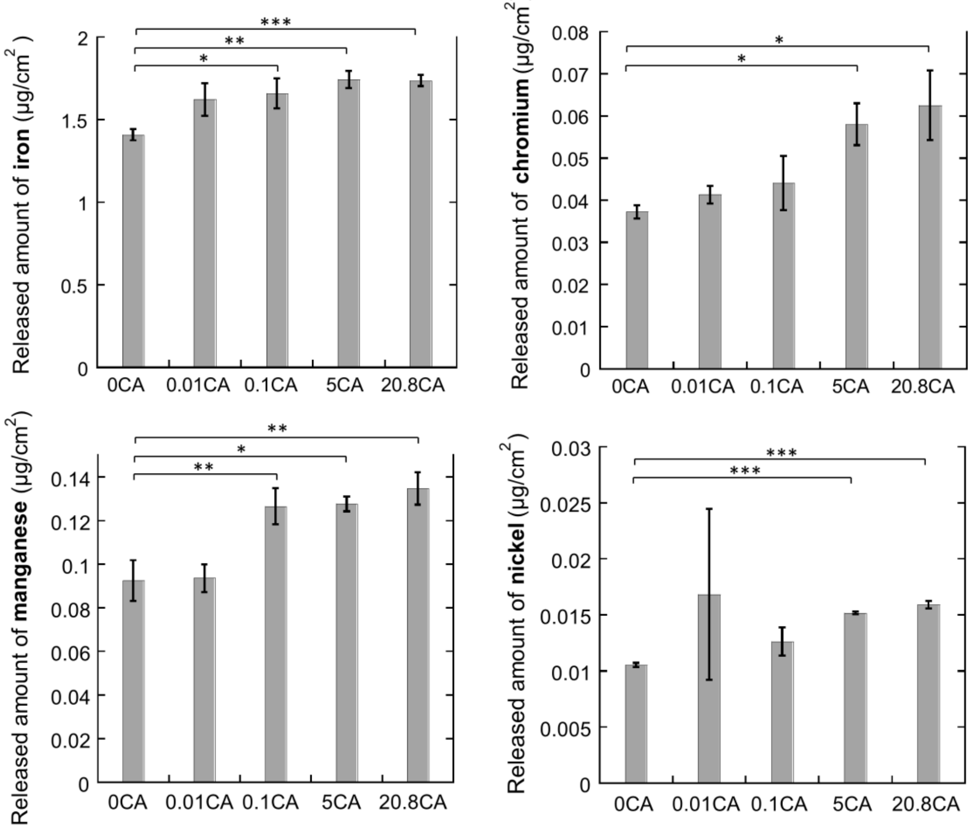
Abraded and as-received surfaces show similar release patterns and enrichment of chromium in the surface oxide upon exposure in citric acid.





Mazinanian N, Odnevall Wallinder I, Hedberg Y. Comparison of the influence of citric acid and acetic acid as simulant for acidic food on the release of alloy constituents from stainless steel AISI 201, J Food Eng 2015: **145**: 51-63.

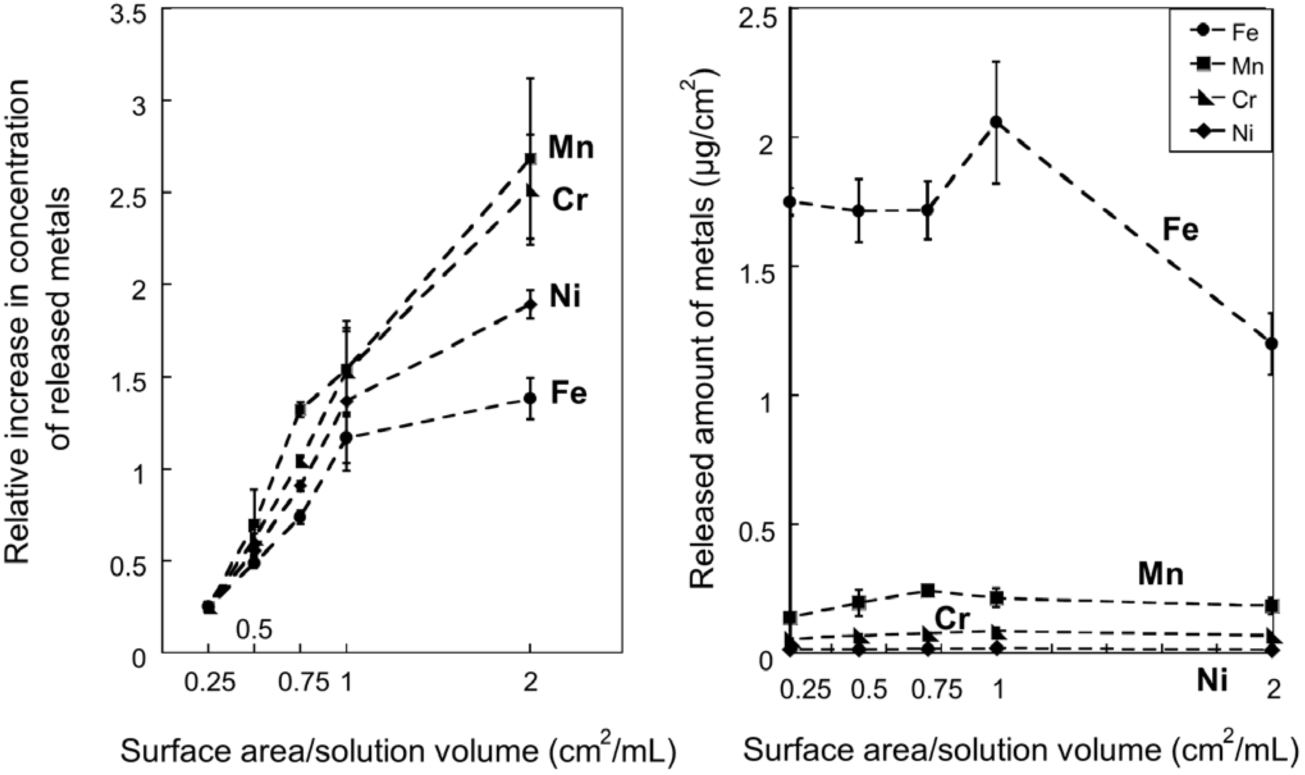
Citric acid as the food simulant is a more aggressive solution from a metal release perspective compared with acetic acid, primarily due to its higher metal binding ability.



Mazinanian N, Odnevall Wallinder I, Hedberg Y. Comparison of the influence of citric acid and acetic acid as simulant for acidic food on the release of alloy constituents from stainless steel AISI 201, J Food Eng 2015: **145**: 51-63.

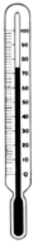
ROYAL INSTITUTE OF TECHNOLOGY

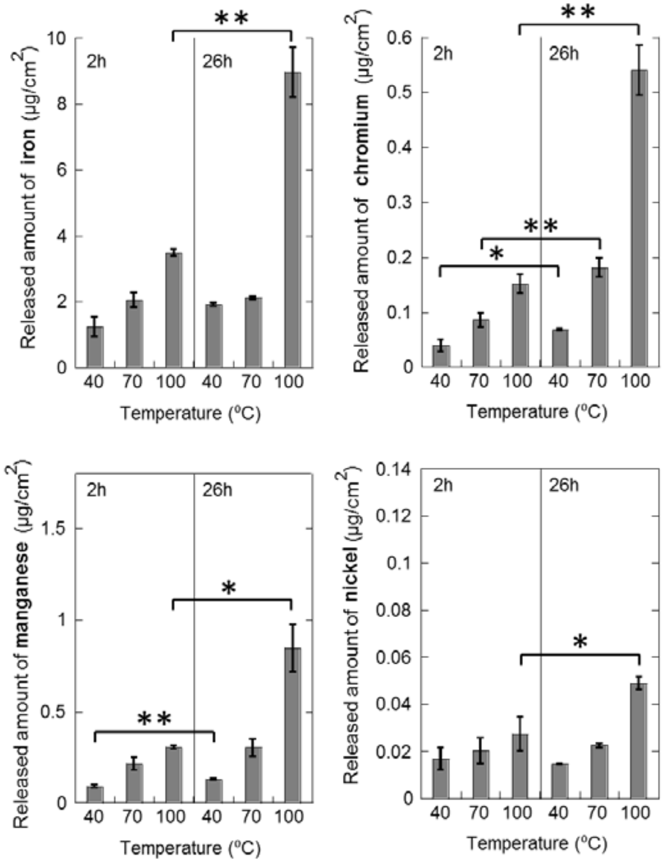
A relatively linear relation between released concentrations of alloy constituents from grade 201 and surface area to solution volumes between 0.25 and 1 cm^2/mL.

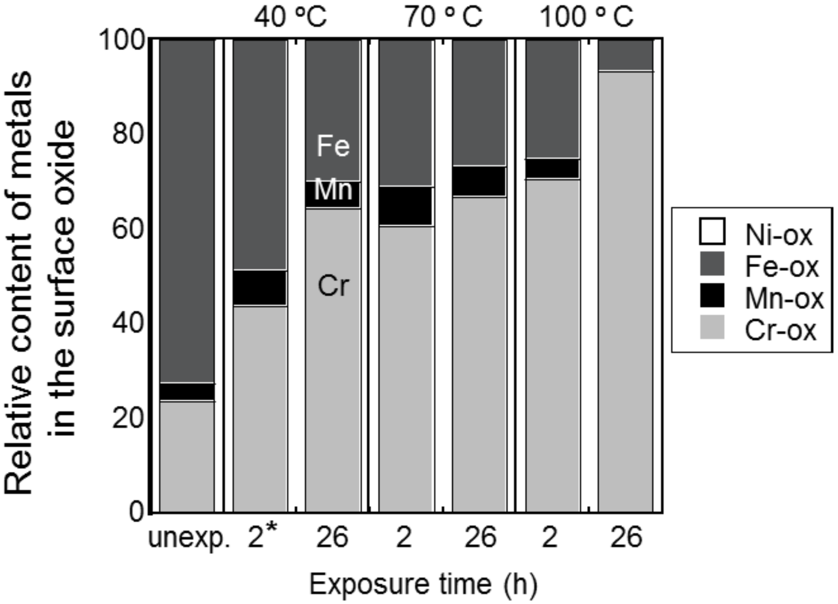


Mazinanian N, Odnevall Wallinder I, Hedberg Y. Comparison of the influence of citric acid and acetic acid as simulant for acidic food on the release of alloy constituents from stainless steel AISI 201, J Food Eng 2015: **145**: 51-63.

Exposures in solutions at 100 °C increase the amount of released metals compared with lower temperatures despite the enrichment of Cr in the surface oxide.

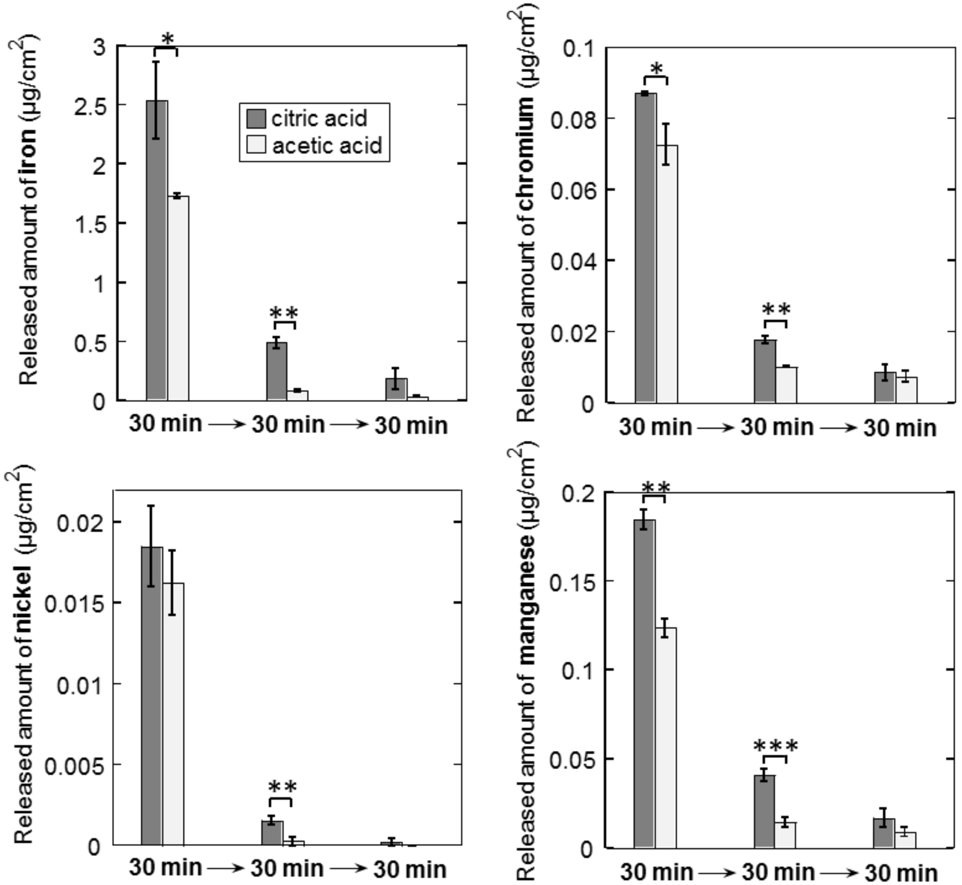






Mazinanian N, Odnevall Wallinder I, Hedberg Y. Comparison of the influence of citric acid and acetic acid as simulant for acidic food on the release of alloy constituents from stainless steel AISI 201, J Food Eng 2015: **145**: 51-63.

Repeated immersion results in lower released amounts of metals and improved barrier properties of the surface oxide with time.



Mazinanian N, Odnevall Wallinder I, Hedberg Y. Comparison of the influence of citric acid and acetic acid as simulant for acidic food on the release of alloy constituents from stainless steel AISI 201, J Food Eng 2015: **145**: 51-63.

ROYAL INSTITUTE
OF TECHNOLOGY

Appendix-2

Metal release from different grades of stainless steel in food-relevant solutions.
Influence of solution, test protocol, surface finish, and repeated exposure
- a comparison with previous KTH data.

Investigated materials.

	grade	C	Cr	Ni	Mn	Mo	Si	P	S	N	Surface finish
From ref. 1	2205^{D*}	0.022	22.5	5.6	1.7	3.1	0.31	0.020	0.001	0.15	2B
	201^{A**}	0.034	17.6	4.2	6.5	0.41	0.42	0.026	0.001	-	Shot-blasted
	304^{A**}	0.047	18.1	9.0	1.1	0.31	0.33	0.026	0.002	-	2B
	310^{A**}	0.056	24.2	19.1	0.9	0.23	0.37	0.019	0.001	-	2R
	$316L^{A**}$	0.032	16.6	10.6	1.0	2.1	0.40	0.024	0.001	-	2B
	409^{F***}	0.015	11.4	0.11	0.30	-	0.43	0.016	0.002	-	2B
	430^{F***}	0.040	16.0	0.22	0.48	0.064	0.27	0.017	0.002	-	2R
On-going study	201^{A**}	0.107	16.94	3.59	5.77	0.21	0.65	0.033	0.002	0.15	2D
	304^{A**}	0.038	17.89	9.03	1.17	0.36	0.42	0.027	0.003	0.04	2B

* D=Duplex, ** A=Austenitic, *** F=Ferritic

Surface finishes	description
2B	Cold rolling, heat treatment, pickling and skin passing
2D	Cold rolling, heat treatment, pickling
2R	Cold rolling and bright annealing
Shot-blasted	Cold rolling, heat treatment, pickling and skin passing, shot blasted with steel grit and then pickled

Generally decreasing surface roughness: 2D > 2B > 2R

---

[1] G. Herting , I. Odnevall Wallinder, C. Leygraf (2007), Metal release from various grades of stainless steel exposed to synthetic body fluids, Corrosion Science 49: 103–111

Synthetic fluids and exposure conditions.

Exposures at
8 and 26 h (70 (2h) / 40 °C),
CoE protocol

Citric acid, pH 2.4 (CA 2.4)
5 g/L citric acid

Citric acid, pH 4.5 (CA 4.5)
20.8 g/L citric acid + 6 g/L NaOH (pH 4.5)

Artificial tap water, pH 7.5 (TW)
0.12 g/L $NaHCO_3$, 0.07 g/L $MgSO_4 \cdot 7H_2O$,
0.12 g/L $CaCl_2 \cdot 2H_2O$

Exposure at
37 °C [1]

Artificial lysosomal fluid, pH 4.5 (ALF)
20.8 g/L citric acid, 6 g/L NaOH, etc.

Exposure at
40 and 100 °C [2]

Acetic acid, pH 2.4 (Italian law)

---

[1] G. Herting et al. 2007, Metal release from various grades of stainless steel exposed to synthetic body fluids, Corros. Sci. 49: 103–111

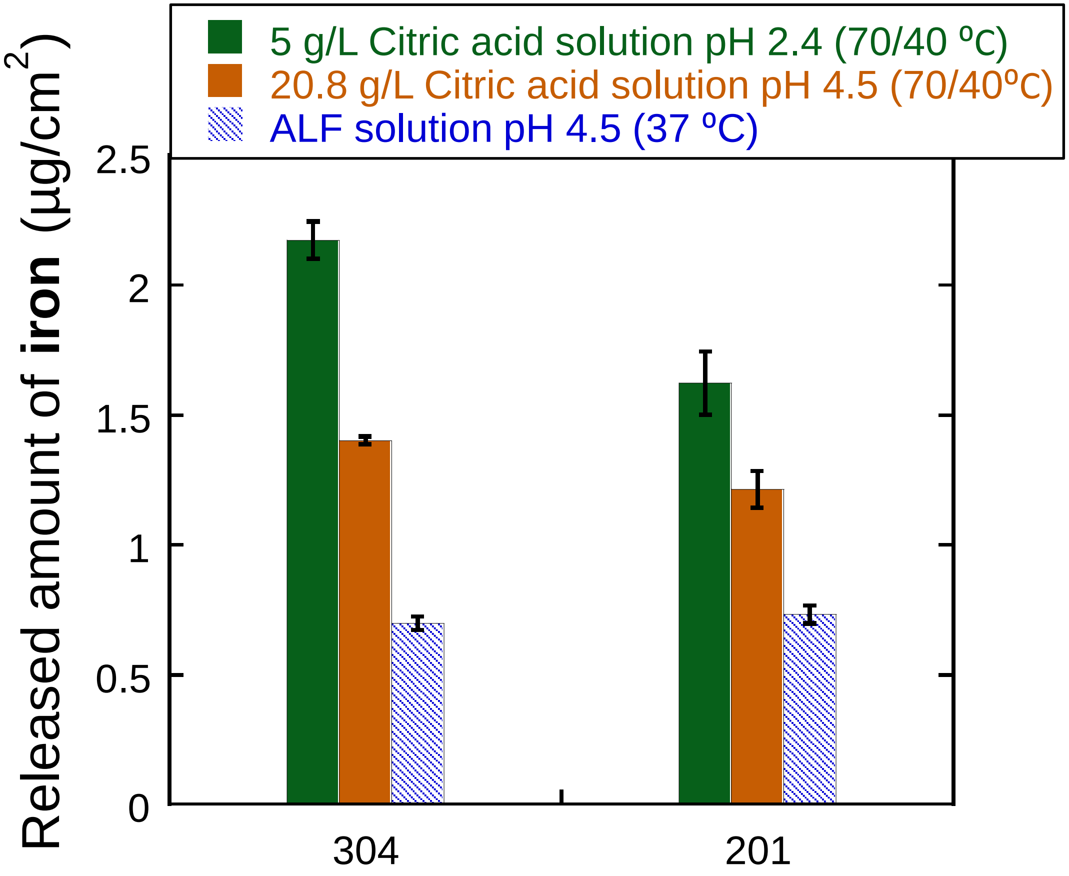
[2] G. Herting et al. 2008, Corrosion-induced release of chromium and iron from ferritic stainless steel grade AISI 430 in simulated food contact, J. Food Engineering 87: 291–300

Higher release of Fe from grades 304 and 201 in citric acid (pH 2.4, 70/40 °C, CoE protocol) compared with ALF (pH 4.5, 37 °C).

ROYAL INSTITUTE OF TECHNOLOGY

As-received 304 and 201
ALF 24 h at 37 °C
Citric acid solutions 26 h at (70/40 °C)

ALF – artificial lysosomal fluid (pH 4.5)

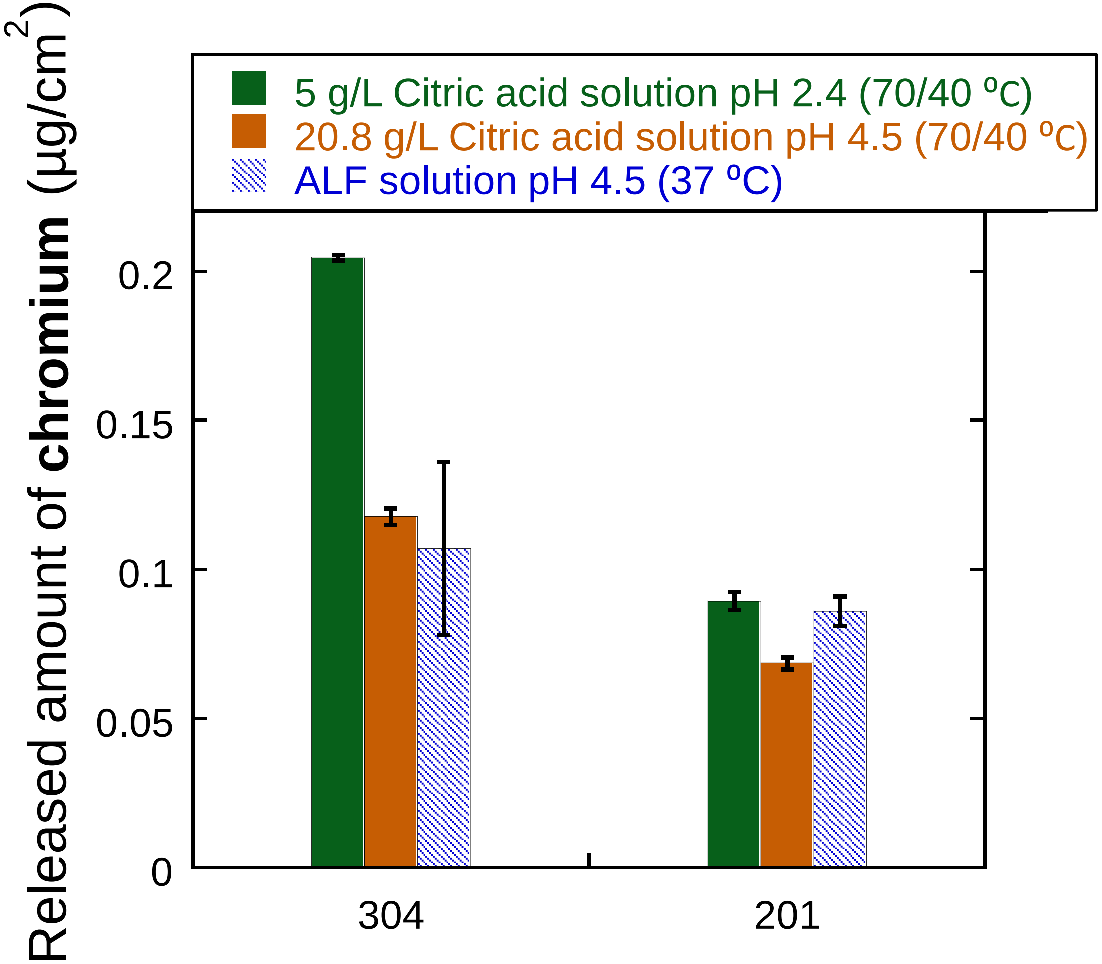


G. Herting , I. Odnevall Wallinder, C. Leygraf (2007), Metal release from various grades of stainless steel exposed to synthetic body fluids, Corrosion Science 49: 103–111

Higher or comparable release of Cr from grades 304 and 201 in citric acid (pH 2.4, 70/40 °C, CoE protocol) compared with ALF (pH 4.5, 37 °C).

As-received 304 and 201
ALF 24 h at 37 °C
Citric acid solutions 26 h at (70/40 °C)

ALF – artificial lysosomal fluid (pH 4.5)



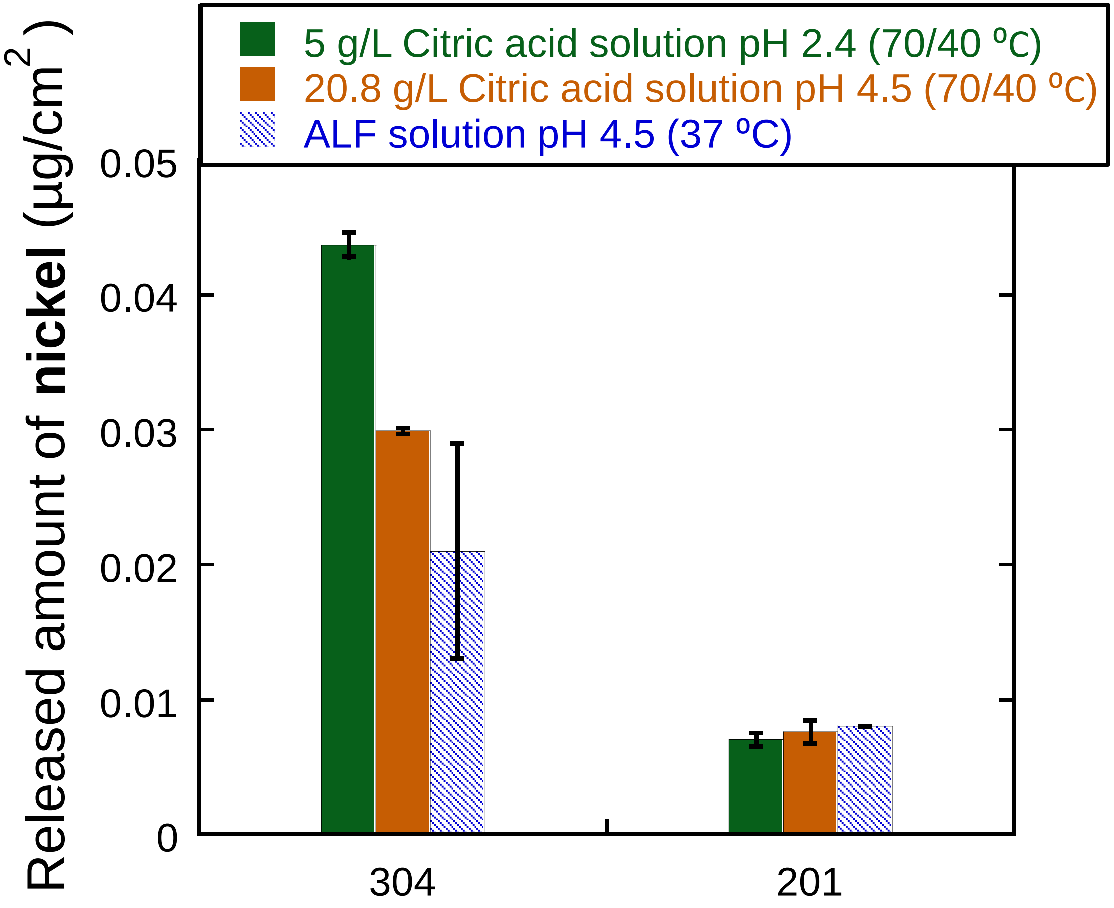
G. Herting , I. Odnevall Wallinder, C. Leygraf (2007), Metal release from various grades of stainless steel exposed to synthetic body fluids, Corrosion Science 49: 103–111

ROYAL INSTITUTE
OF TECHNOLOGY

Higher or comparable release of Ni from grades 304 and 201 in citric acid (pH 2.4, 70/40 °C, CoE protocol) compared with ALF (pH 4.5, 37 °C).

As-received 304 and 201
ALF 24 h at 37 ^{o}C
Citric acid solutions 26 h at (70/40 ^{o}C)

ALF – artificial lysosomal fluid (pH 4.5)

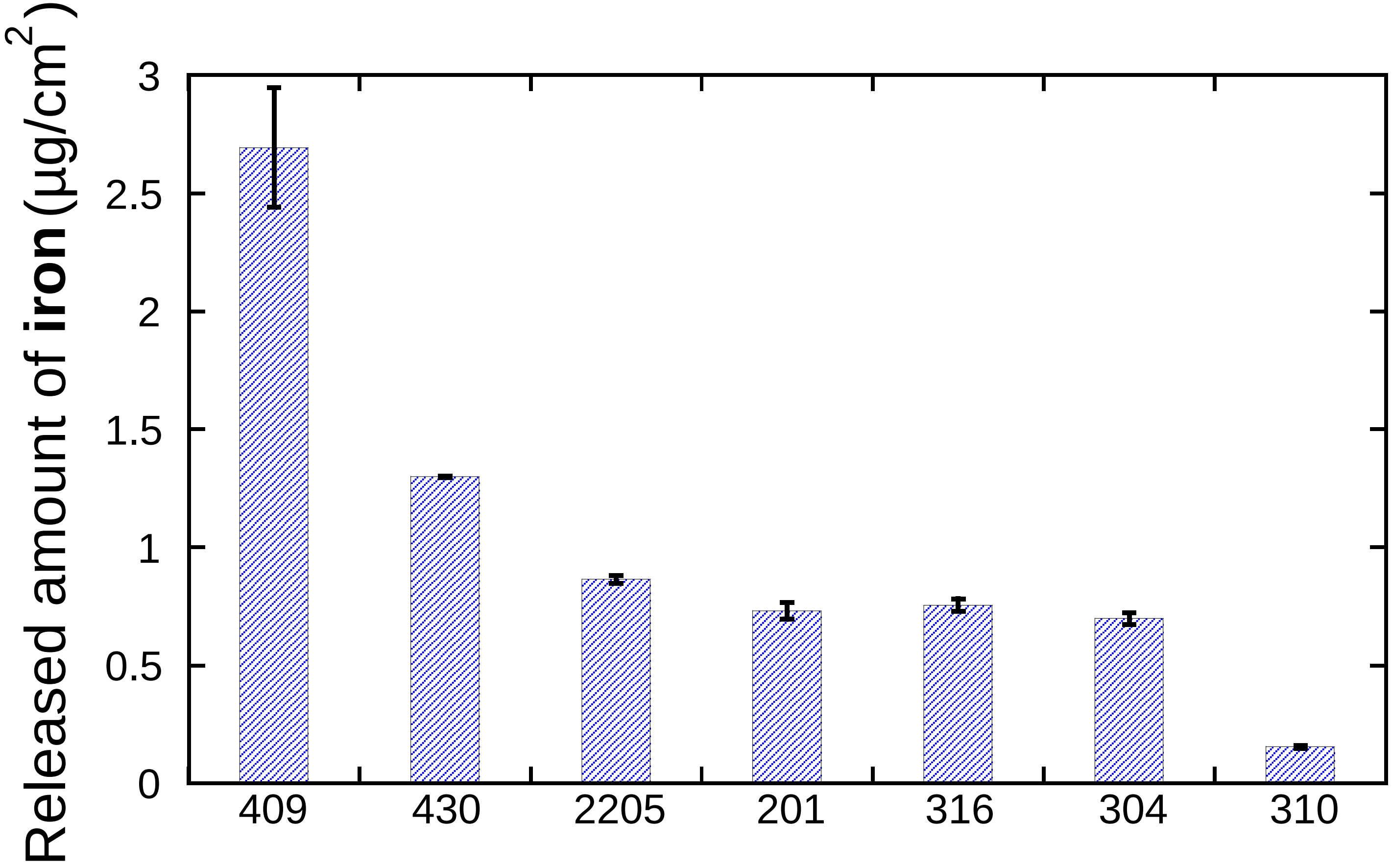


Ref. [1] G. Herting , I. Odnevall Wallinder, C. Leygraf (2007), Metal release from various grades of stainless steel exposed to synthetic body fluids, Corrosion Science 49: 103–111

The release of Fe from grades 304 and 201 was lower compared with the ferritic grades but comparable with the duplex and austenitic grades (except 310).

As-received
37 °C
ALF (pH 4.5)
24 h

ALF – artificial lysosomal fluid



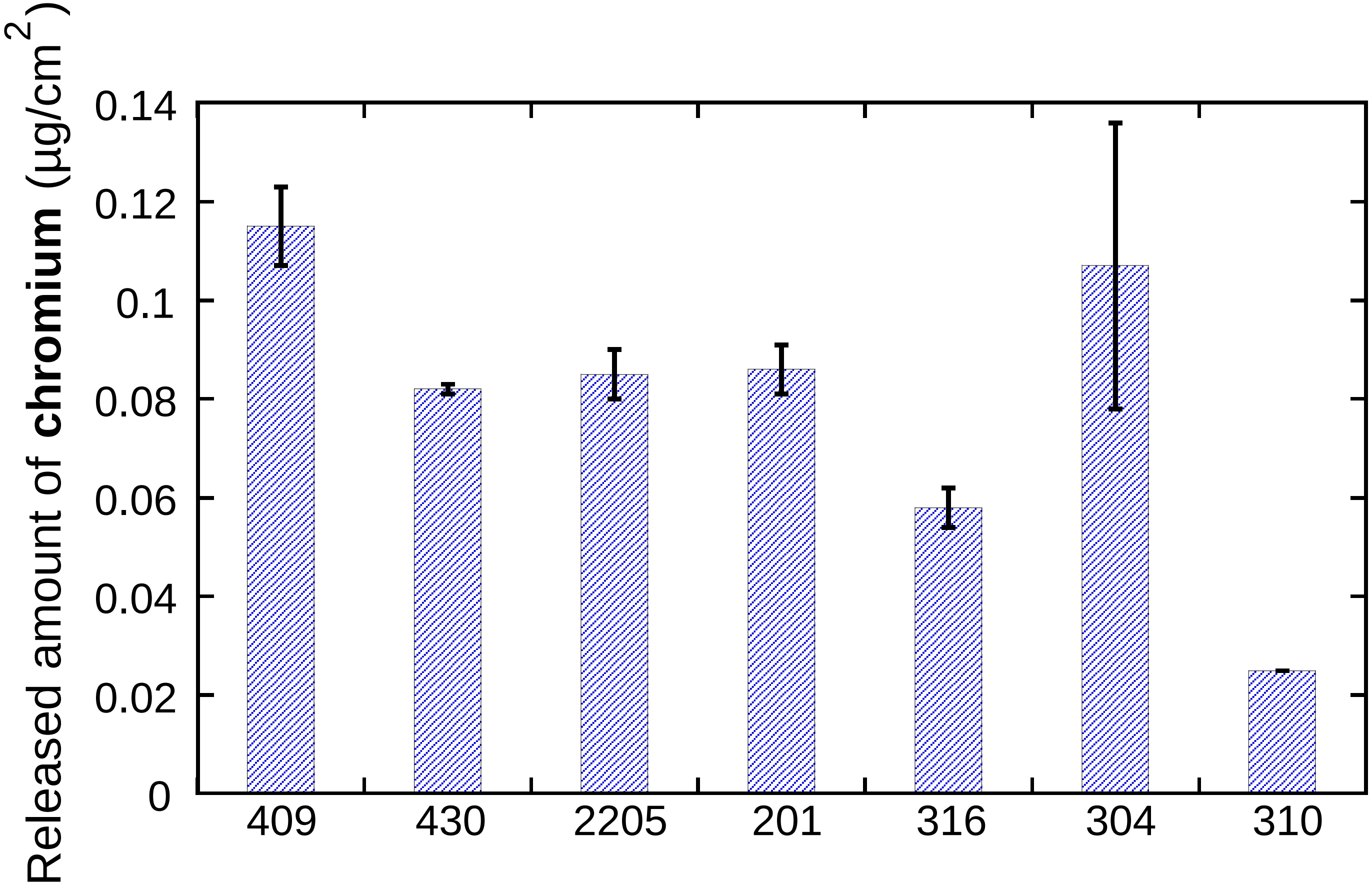
409 > 430 > 2205 ≥ 201 ≈ 316 ≈ 304 >> 310

G. Herting , I. Odnevall Wallinder, C. Leygraf (2007), Metal release from various grades of stainless steel exposed to synthetic body fluids, Corrosion Science 49: 103–111

Low released amounts of Cr from grades 304 and 201, but comparable with the ferritic, duplex and austenitic grades (except 310).

As-received
37 °C
ALF (pH 4.5)
24 h

ALF – artificial lysosomal fluid

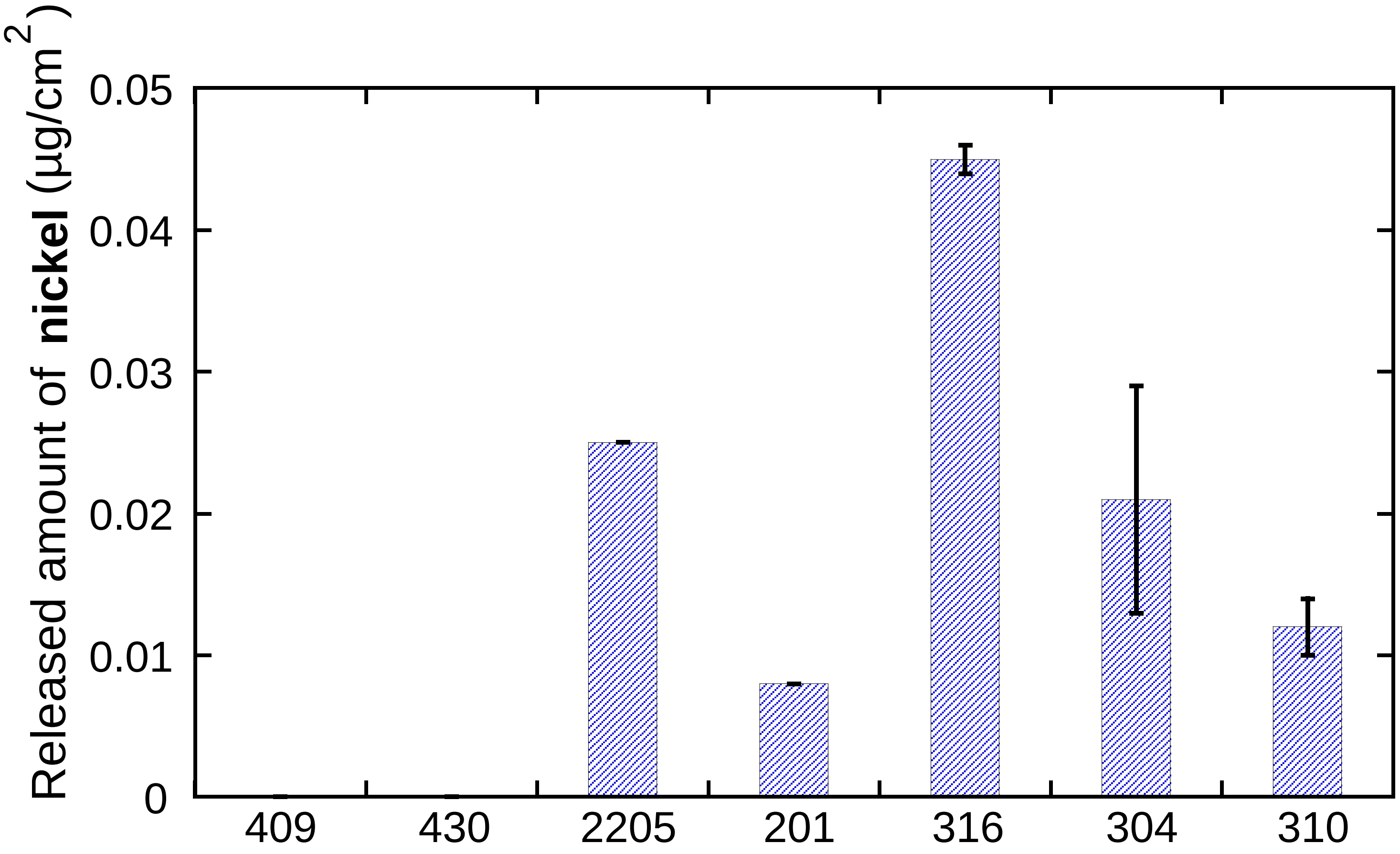


G. Herting , I. Odnevall Wallinder, C. Leygraf (2007), Metal release from various grades of stainless steel exposed to synthetic body fluids, Corrosion Science 49: 103–111

Very low amounts of released Ni from grade 201 and lower compared with the duplex and other austenitic grades.

As-received
37 °C
ALF (pH 4.5)
24 h

ALF – artificial lysosomal fluid

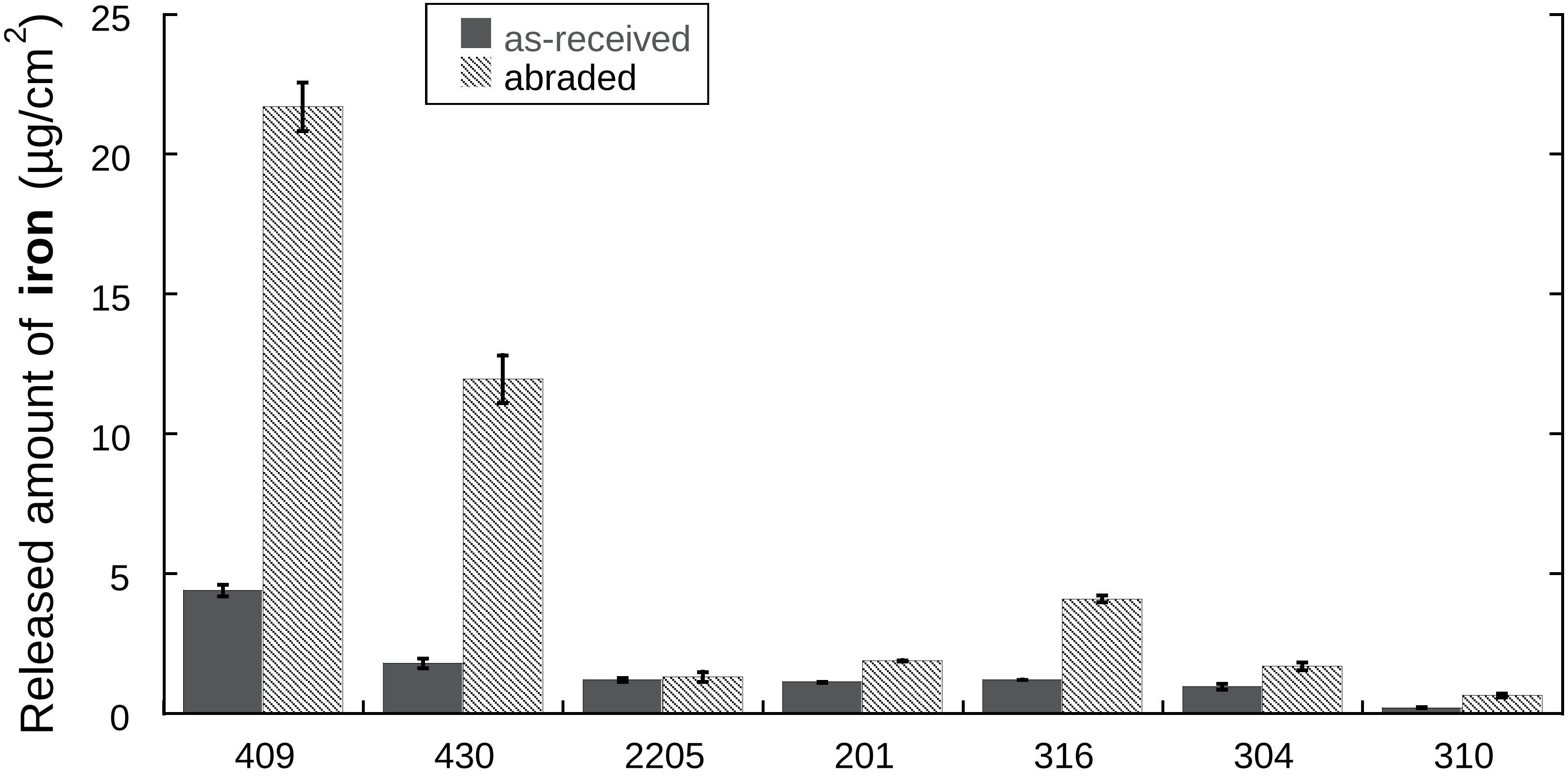


G. Herting , I. Odnevall Wallinder, C. Leygraf (2007), Metal release from various grades of stainless steel exposed to synthetic body fluids, Corrosion Science 49: 103–111

More Fe released from abraded surfaces compared with as-received surfaces, independent of grade.

37 °C
ALF
(pH 4.5)
168 h

ALF – artificial lysosomal fluid

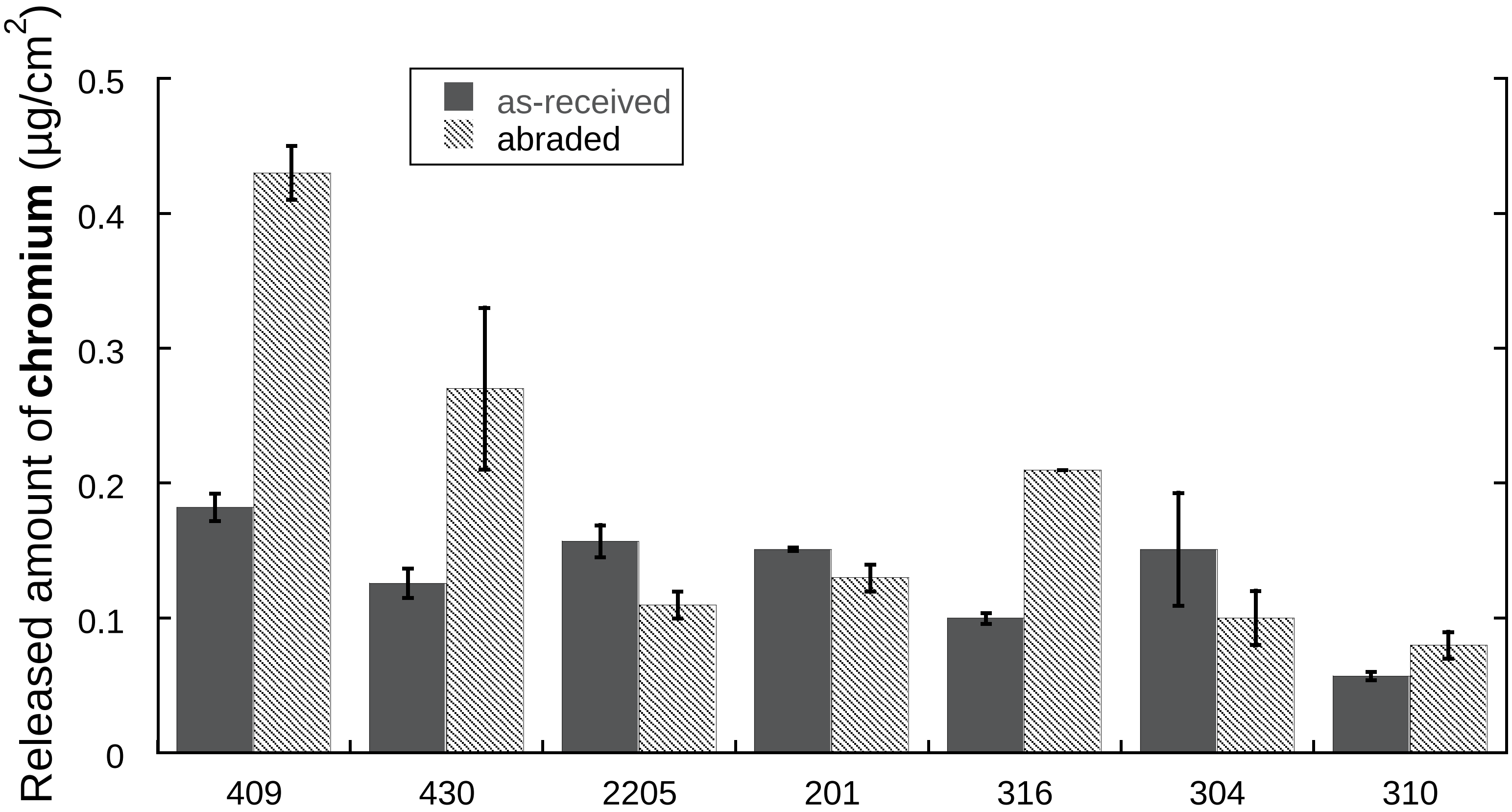


G. Herting , I. Odnevall Wallinder, C. Leygraf (2007), Metal release from various grades of stainless steel exposed to synthetic body fluids, Corrosion Science 49: 103–111

Higher or similar amounts of released Cr from abraded surfaces compared with as-received surfaces.

37 °C
ALF
(pH 4.5)
168 h

ALF – artificial lysosomal fluid



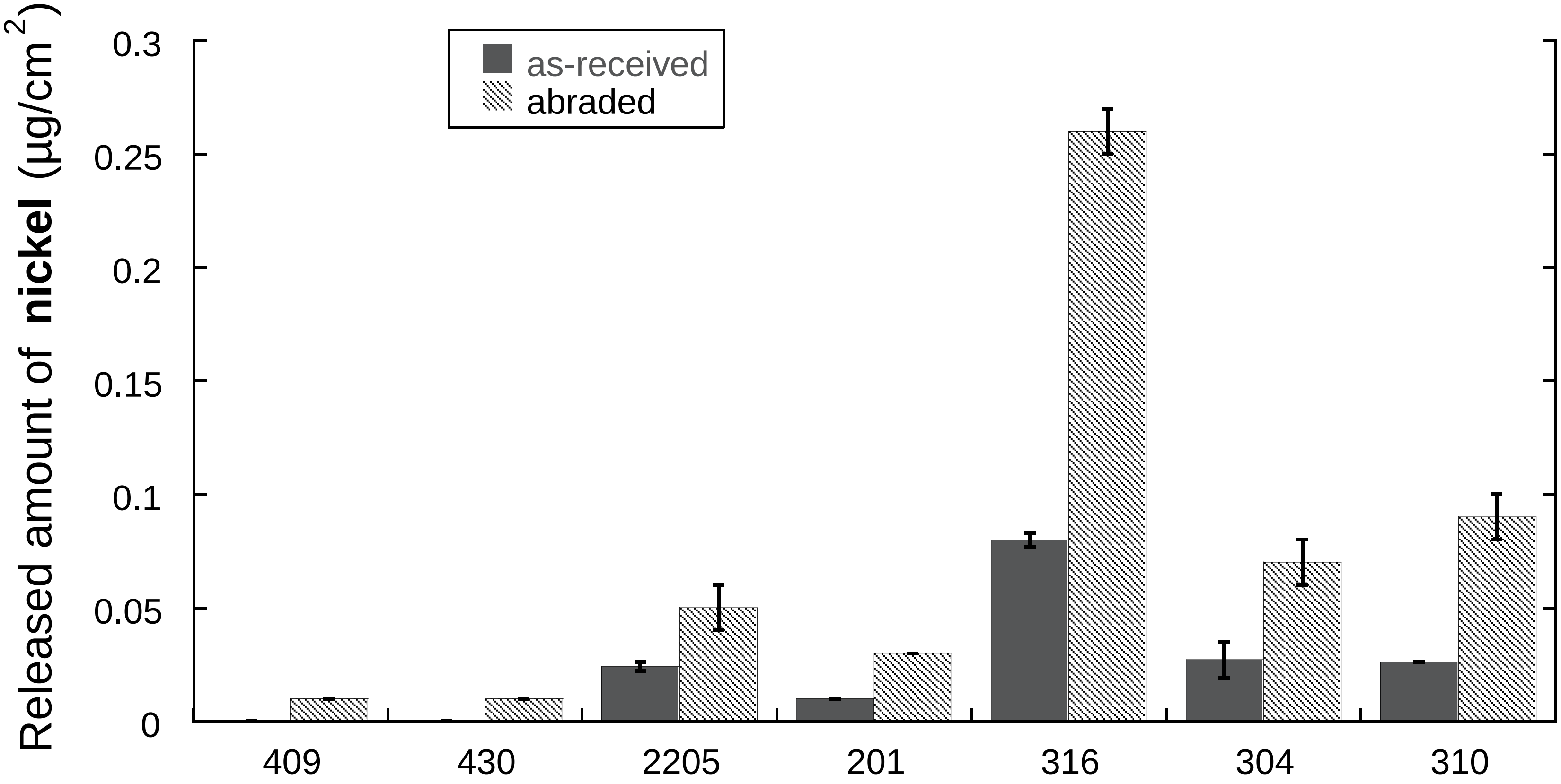
G. Herting , I. Odnevall Wallinder, C. Leygraf (2007), Metal release from various grades of stainless steel exposed to synthetic body fluids, Corrosion Science 49: 103–111

ROYAL INSTITUTE
OF TECHNOLOGY

More Ni released from abraded surfaces compared with as-received surfaces, independent of grade.

37 °C
ALF
(pH 4.5)
168 h

ALF – artificial lysosomal fluid



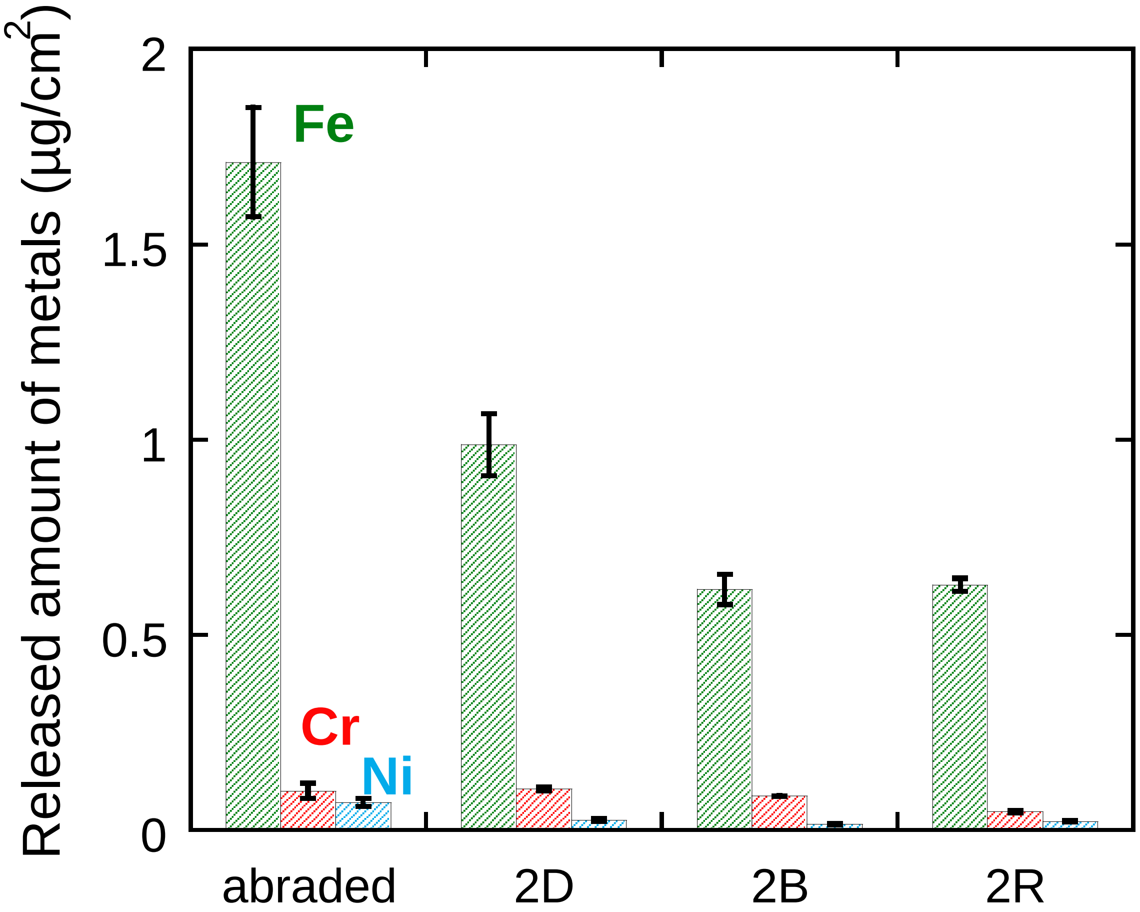
G. Herting , I. Odnevall Wallinder, C. Leygraf (2007), Metal release from various grades of stainless steel exposed to synthetic body fluids, Corrosion Science 49: 103–111

ROYAL INSTITUTE
OF TECHNOLOGY

The release of metals depends on the surface finish. The release of Fe from grade 304 decreased according to: abraded > 2D > 2B ≈ 2R.

304
37 °C
ALF (pH 4.5)
168 h

ALF – artificial lysosomal fluid

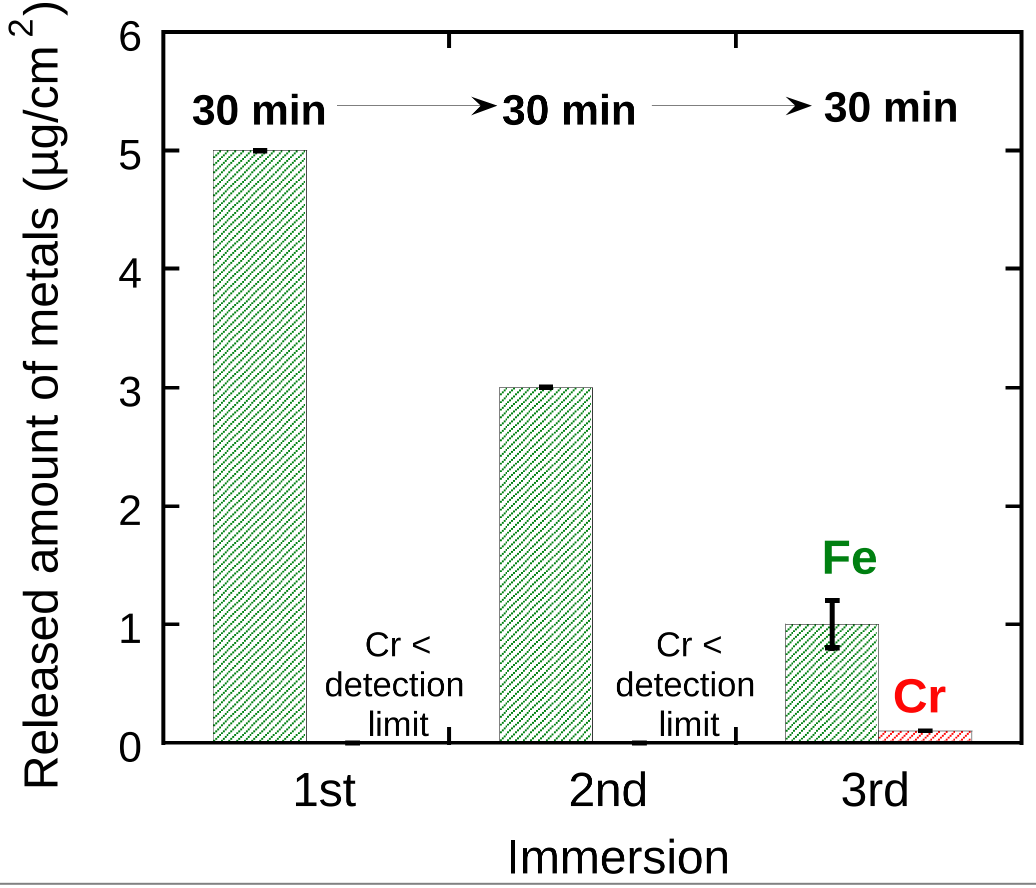


G. Herting , I. Odnevall Wallinder, C. Leygraf (2007), Metal release from various grades of stainless steel exposed to synthetic body fluids, Corrosion Science 49: 103–111

The release of metals depends on prevailing experimental set-up. The release of Fe from grade 430 in acetic acid (pH 2.4) reduced upon repeated exposure to fresh solution at 100 °C.

430
abraded
100 °C
Acetic acid
(pH 2.4)

ALF – artificial lysosomal fluid

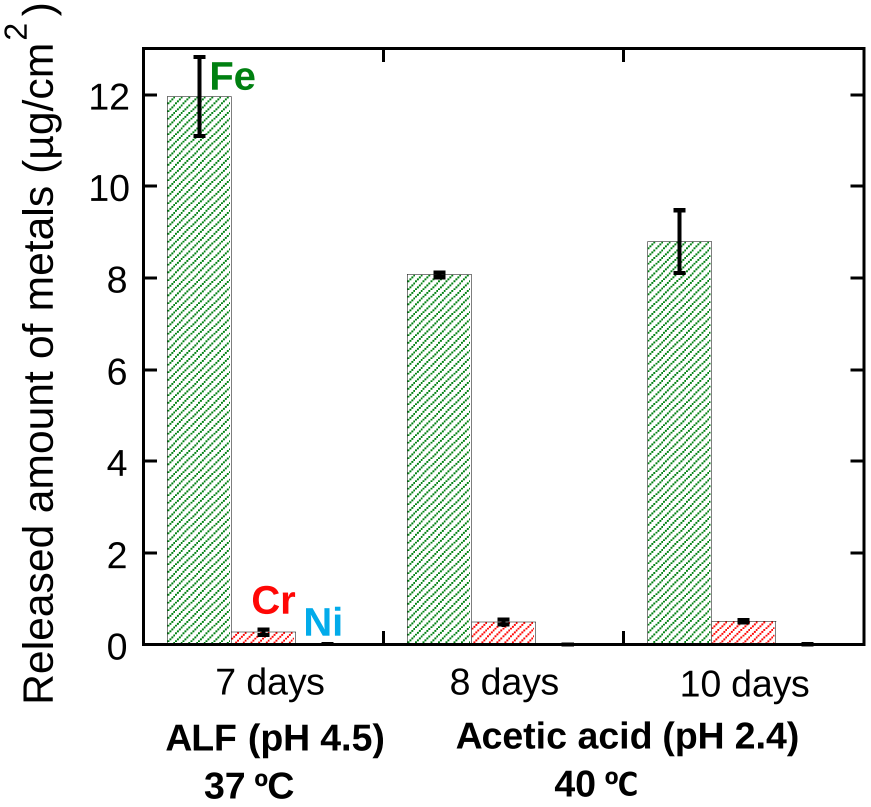


G. Herting et al. 2008, Corrosion-induced release of chromium and iron from ferritic stainless steel grade AISI 430 in simulated food contact, J. Food Engineering 87: 291–300

The release of metals depends on the solution characteristics. More Fe released from grade 430 in the solution of ALF (pH 4.5) compared with acetic acid of lower pH (2.4).

430
Abraded

ALF – artificial lysosomal fluid



<u>ALF:</u> G. Herting , I. Odnevall Wallinder, C. Leygraf (2007), Metal release from various grades of stainless steel exposed to synthetic body fluids, Corrosion Science 49: 103–111

<u>Acetic acid:</u> G. Herting , I. Odnevall Wallinder, C. Leygraf (2008), Corrosion-induced release of chromium and iron
from ferritic stainless steel grade AISI 430 in simulated food contact, Journal of Food Engineering 87: 291–300

ROYAL INSTITUTE OF TECHNOLOGY

The solution aggressivity governs to a large extent the metal release process.

KEY MESSAGES

Citric acid (5 g/L, pH 2.4) the most aggressive solution.
CoE protocol more aggressive compared with Italian law.

CA 2.4 $^{(T=70\ °C+40\ °C)}$ > CA 4.5 $^{(T=70\ °C+40\ °C)}$ > ALF 4.5 $^{(T=37\ °C)}$
> acetic acid 2.4 $^{(T=40\ °C)}$ >> TW 7.5 $^{(T=70\ °C+40\ °C)}$

CA – Citric acid
ALF – Artificial lysosomal fluid
TW – Artificial tap water

ROYAL INSTITUTE
OF TECHNOLOGY

Appendix-3

Detection limits and recovery of Fe, Cr, Mn, Ni, and Mo in artificial tap water (pH 7.5) and citric acid (pH 2.4) using Graphite Furnace Atomic Absorption Spectroscopy.

ROYAL INSTITUTE
OF TECHNOLOGY

Limits of detection (LOD)* for Fe, Cr, Mn, Ni, and Mo in artificial tap water (pH 7.5) and citric acid (pH 2.4).

elements	LOD in artificial tap water (pH 7.5) [µg/cm^2]	LOD in citric acid (pH 2.4) [µg/cm^2]
Fe	0.0002	0.0004
Ni	0.0004	0.0002
Cr	0.00004	0.00007
Mn	0.0001	0.0002
Mo	0.0002	0.0001

1 µg/cm² corresponds to 1000 µg/L at the standard loading of this study (1 cm²/mL)

**calculated as 3 x average standard deviations of blank sample*

The limit of quantification (LOQ), above which a value has approximately < 30% error, is estimated to be 10 times the LOD. It is hence ≤ 0.004 µg/cm² or ≤ 4 µg/L for all elements and solutions.

ROYAL INSTITUTE
OF TECHNOLOGY

Recovery tests for Cr in both citric acid (pH 2.4) and artificial tap water (pH 7.5).

Test solutions and concentrations	Recovery (%)*
citric acid solution (pH 2.4)	90.7
5 µg/L Cr in citric acid (pH 2.4)	99.9
10 µg/L Cr in citric acid (pH 2.4)	96.0
15 µg/L Cr in citric acid (pH 2.4)	101.3
30 µg/L Cr in citric acid (pH 2.4)	104.6
50 µg/L Cr in citric acid (pH 2.4)	111.5
60 µg/L Cr in citric acid (pH 2.4)	104.5
100 µg/L Cr in citric acid (pH 2.4)	113.4
Artificial tap water solution (pH 7.5)	96.2
20 µg/L Cr in artificial tap water (pH 7.5)	96.1
60 µg/L Cr in artificial tap water (pH 7.5)	91.8

* Recovery (%) must be in the range of 85-115 %

ROYAL INSTITUTE
OF TECHNOLOGY

Recovery tests for Fe, Mn, and Ni in citric acid (pH 2.4).

Test solutions and concentrations	Recovery (%)*
50 µg/L Fe in citric acid (pH 2.4)	97
100 µg/L Fe in citric acid (pH 2.4)	94.1
150 µg/L Fe in citric acid (pH 2.4)	107.4
200 µg/L Fe in citric acid (pH 2.4)	96.1
10 µg/L Mn in citric acid (pH 2.4)	100.3
15 µg/L Mn in citric acid (pH 2.4)	102.9
30 µg/L Mn in citric acid (pH 2.4)	100.2
60 µg/L Mn in citric acid (pH 2.4)	91.4
10 µg/L Ni in citric acid (pH 2.4)	101
15 µg/L Ni in citric acid (pH 2.4)	90.3
30 µg/L Ni in citric acid (pH 2.4)	100.8
60 µg/L Ni in citric acid (pH 2.4)	105
100 µg/L Ni in citric acid (pH 2.4)	106.9

* Recovery (%) must be in the range of 85-115 %

ROYAL INSTITUTE
OF TECHNOLOGY

Appendix-4
Typical loadings in food applications.

How is ”surface area / solution volume ratio” calculated?

Based on **the CoE protcol**, for articles that can be filled, the test condition is defined as:

” The article should be filled with the simulant to approximately ⅔ total capacity and then suitably covered to reduce evaporation.”[1]

Therefore, ”surface area / solution volume ratio” is:
the total exposed surface area (to $\frac{2}{3}$ volume) /$\frac{2}{3}$ volume

For a cylinder without considering its upper circle (the lid of pot in our case), then we have:
”surface area / solution volume ratio” = $[(\frac{4}{3}\pi rh + \pi r^2) / \frac{2}{3}(\pi r^2 h)]$

---

[1] *CoE protocol (2013). Metals and alloys used in food contact materials and articles, a practical guide for manufacturers and regulators (first ed). European Directorate for the Quality of Medicines & HealthCare (EDQM), France, Chapter 3, page 182*

Example 1

Dimensions*	”surface area / solution volume ratio” (1/cm)
Diameter (2r): 15 cm Height (h) : 7 cm	0.48

∗ http://www.ikea.com/se/sv/catalog/products/60129726/

Example 2

Dimensions*	”surface area / solution volume ratio” (1/cm)
Diameter (2r): 20 cm Height (h) : 13 cm	0.32

∗ http://www.ikea.com/se/sv/catalog/products/30101154/

Example 3

Dimensions*	”surface area / solution volume ratio” (1/cm)
Diameter (2r): 23 cm Height (h) : 10.5 cm	0.32

* http://www.ikea.com/se/sv/catalog/products/60083554/

Example 4

Dimensions*	”surface area / solution volume ratio” (1/cm)
Diameter (2r): 19 cm Height (h) : 13 cm	0.33

* http://www.ikea.com/se/sv/catalog/products/10129724/

Example 5

Dimensions*	”surface area / solution volume ratio” (1/cm)
Diameter (2r): 25 cm Height (h) : 2 cm	0.91

* http://www.ikea.com/se/sv/catalog/products/90208208/

Example 6

Dimensions*	”surface area / solution volume ratio” (1/cm)
Diameter (2r): 24 cm Height (h) : 4 cm	0.54

* http://www.ikea.com/se/sv/catalog/products/96225800/

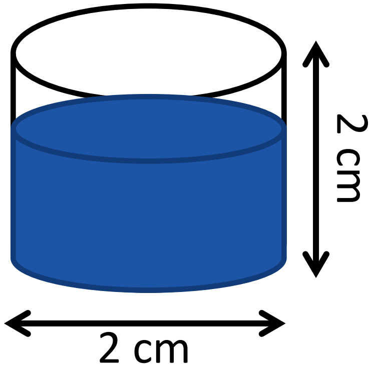
Example 7

Dimensions*	”surface area / solution volume ratio” (1/cm)
Diameter (2r): 4 cm Height (h) : 4 cm	1.4

Diameter (2r): 4 cm
Height (h) : 4 cm

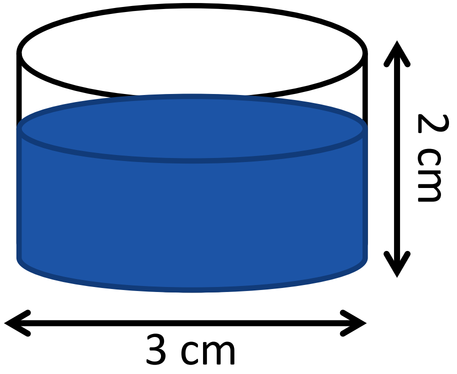
* http://www.ikea.com/se/sv/catalog/products/70208129/
** http://www.ikea.com/se/sv/catalog/products/00133038/

Example 8



Dimensions	”surface area / solution volume ratio” (1/cm)
Diameter (2r): 2 cm Height (h) : 2 cm	2.75

Example 9



Dimensions	”surface area / solution volume ratio” (1/cm)
Diameter (2r): 3 cm Height (h) : 2 cm	2.1

KEY MESSAGE

Based on the Italian law text, ”adopt a surface-to-volume ratios as close as possible to the real value and in any case between 2 and 0.5.” [2]

In reality, ”surface area/ solution volume ratio” < 0.5 (1/cm) is also common and possible!

Therefore, ”surface area/ solution volume ratio” range of 0.25 to 2 (1/cm) was chosen in the loading experiments

---

[2] The Italian law text, 21-03-1973, D.M., (1973).