

Metal Release and Corrosion of Stainless Steel in Simulated Food Contact

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Abstract

Knowledge on metal release behaviour of stainless steels used in food processing applications and cooking utensils is essential within the framework of human health risk assessments. Recently, a new European test guideline (the CoE protocol) has been implemented to ensure safety of metals and alloys in food contact, such as stainless steels. This guideline suggests 5 gL⁻¹ citric acid (pH 2.4) as a food simulant for acidic foods of pH ≤ 4.5. So far, limited assessments exist that investigate the correlation between the bioaccessibility, material characteristics, corrosion behaviour and surface chemistry of stainless steel for food application tests using citric acid. Therefore, this doctoral thesis comprises an in-depth interdisciplinary and multi-analytical research effort to fill this knowledge gap.

This work includes thorough investigations of a range of stainless steel grades in simulated food contact as a function of different important parameters such as grades, surface finish, temperature, pH, solution composition, metal complexation and buffering capacity, concentration of the complex forming agents, loading, and repeated usage. This is accomplished by kinetic studies of metal release, electrochemical, and surface analytical investigations. Another focus of this thesis is to assess the dominating metal release process in citric acid or chloride containing solutions of varying pH.

This study suggests protonation (at acidic pH) and surface complexation (at weakly acidic and neutral pH) as the predominant metal release mechanisms for stainless steel in citric acid solutions. Solution complexation may also play a role by hindering metal precipitation at weakly acidic and neutral pH, and metal release from surface defects / inclusions may initially be important for non-passivated surfaces.

Sammanfattning

Kunskap om metallfrisättning från rostfritt stål som används i livsmedelsapplikationer och köksredskap är avgörande inom ramen för hälsoriskbedömningar. En ny europeisk riktlinje (CoE protokollet) publicerades 2013 för att garantera säkerheten för metaller och legeringar i livsmedelskontakt, t.ex. rostfritt stål. Denna riktlinje föreslår 5 gL^{-1} citronsyra (pH 2.4) som en testlösning för sura livsmedel med ett $\text{pH} \leq 4.5$. Hittills finns ett mycket begränsat antal studier som undersöker biotillgänglighet, materialegenskaper, korrosionsbeteende och ytkemi av rostfritt stål i kontakt med citronsyra. Denna kunskapslucka fylls i denna doktorsavhandling genom djupgående tvärvetenskapliga och multianalytiska studier.

I detta arbete undersöks hur olika rostfria stålsorter beter sig i simulerad livsmedelskontakt som funktion av olika parametrar som stålsort, ytråhet, temperatur, pH, lösningssammansättning, komplexerings- och buffertkapacitet, koncentration av komplexbildande komponenter, samt förhållandet mellan yta och lösningsvolym, och upprepad användning. Detta görs genom kinetiska studier av metallfrisättningsprocessen, elektrokemiska undersökningar, och ytanalyser. Dessutom undersöks den dominerande metallfrisättningsprocessen i citronsyra och i kloridlösningar av varierande pH.

Denna studie visar att protonering (vid surt pH) och ytkomplexering (vid sura och neutrala pH-värden) är de dominerande mekanismerna för metallfrisättning från rostfritt stål i lösningar med citronsyra. Komplexering av frisatta metaller i lösning kan också spela roll genom att hindra metallutfällning vid svagt surt eller neutralt pH. Metallfrisättning från defekter / inneslutningar kan initialt påverka icke-passiverade ytor av rostfritt stål.

List of appended papers

- I. Metal release from stainless steel powders and massive sheets – comparison and implication for risk assessment of alloys**
Y. Hedberg, N. Mazinanian, I. Odnevall Wallinder
Journal of Environmental Science: Processes & Impact, 15: 381 – 392, 2013
- II. Comparison of the influence of citric acid and acetic acid as simulants for acidic food on the release of alloy constituents from stainless steel AISI 201**
N. Mazinanian, I. Odnevall Wallinder, Y. Hedberg
Journal of Food Engineering, 145: 51 – 63, 2015
- III. Metal release and corrosion resistance of different stainless steel grades in simulated food contact**
N. Mazinanian, G. Herting, I. Odnevall Wallinder, Y. Hedberg
Corrosion, 72: 775 – 790, 2016
- IV. Influence of Citric Acid on the Metal Release of Stainless Steels**
N. Mazinanian, I. Odnevall Wallinder, Y. S. Hedberg
Journal of Corrosion Science and Technology, 14: 166 – 171, 2015
- V. Metal Release Mechanisms for Passive Stainless Steel in Citric Acid at Weakly Acidic pH**
N. Mazinanian, Y. S. Hedberg
Journal of the Electrochemical Society, in press

Papers and reports not included in the thesis

VI. Nickel release and surface characteristics of fine powders of nickel metal and nickel oxide in media of relevance for inhalation and dermal contact

N. Mazinianian, Y. Hedberg, I. Odnevall Wallinder

Journal of Regulatory Toxicology and Pharmacology, 65: 135 – 146, 2013

VII. 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

N. Mazinianian, I. Odnevall Wallinder, Y. Hedberg

Technical final report, commissioned by Team Stainless, 2014, available online:

[http://www.worldstainless.org/Files/issf/non-image-files/PDF/KTH/Surface changes and metal release in the presence of citric acid for food applications.pdf](http://www.worldstainless.org/Files/issf/non-image-files/PDF/KTH/Surface_changes_and_metal_release_in_the_presence_of_citric_acid_for_food_applications.pdf)

VIII. Compliance tests of stainless steel as a food contact material using the CoE test guideline

Y. Hedberg, N. Mazinianian, I. Odnevall Wallinder

Technical report for webpage publication, commissioned by Team Stainless, 2014, available online:

[http://www.worldstainless.org/Files/issf/non-image-files/PDF/KTH/Compliance tests of stainless steel as a food contact material using the CoE test guideline e.pdf](http://www.worldstainless.org/Files/issf/non-image-files/PDF/KTH/Compliance_tests_of_stainless_steel_as_a_food_contact_material_using_the_CoE_test_guideline.pdf)

Conference presentations based on this thesis

IX. Influence of citric acid on the extent of metal release from stainless steels

N. Mazinanian, I. Odnevall Wallinder, Y. Hedberg

Proceedings and oral presentation (N. Mazinanian) at the 19th International Corrosion Congress (ICC), November 2 - 6, 2014, Jeju, Korea

X. Stainless Steel in Food Contact: How does citric acid interact with the surface

N. Mazinanian, I. Odnevall Wallinder, Y. Hedberg

Poster presentation, KTH-Sustainability Research Day, October 16, 2014, Stockholm, Sweden

XI. Stainless Steel in Food Contact: How does citric acid interact with the surface

N. Mazinanian, I. Odnevall Wallinder, Y. Hedberg

Poster presentation at Symposium on Surface and Materials Chemistry, Realizing Reformulation, October 22-24, 2014, Lund, Sweden

XII. Stainless Steel in Food Contact: How does citric acid interact with the surface

N. Mazinanian, I. Odnevall Wallinder, Y. Hedberg

Poster presentation at Energy Dialogue 2014, November 20, KTH, 2014, Stockholm, Sweden

XIII. Stainless Steel in Food Contact: How does citric acid interact with the surface

N. Mazinanian, I. Odnevall Wallinder, Y. Hedberg

Poster presentation at ITM PhD Candidate Conference, KTH, April 15-16, 2015, Stockholm, Sweden

Author's contributions to the appended papers

- I.** Major part in experimental work including FEG-SEM, LALLS and AAS analysis, except for XPS investigations and BET analysis. Minor part in planning and design of experimental set-up, data evaluation/ interpretation and preparation of the manuscript.
- II.** All experimental work including AAS, DPAdCSV and OCP, except for XPS investigations, all calculation parts, and student's t-test analysis. Major part in planning and design of experimental set-up, data evaluation/ interpretation and preparation of the manuscript.
- III.** All experimental work including AAS, OCP and Dynamic Polarization measurements, except for XPS investigations and the experimental part related to passivated coupons and their AAS analysis. All calculation parts and major part in planning and design of experimental set-up, data evaluation/ interpretation and preparation of the manuscript.
- IV.** All experimental work including AAS, except for XPS investigations, and all analysis related to the student's t-test. Major part in planning and design of experimental set-up, data evaluation/ interpretation and preparation of the manuscript.
- V.** All experimental work including AAS, except for XPS investigations. All calculation parts, except JESS modelling. Major part in planning and design of experimental set-up, data evaluation/ interpretation and preparation of the manuscript.

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Abbreviations

AES	Auger Electron Spectroscopy
AFM	Atomic Force Microscopy
AISI	American Iron and Steel Institute
ALF	Artificial Lysosomal Fluid
AMI	American Meat Institute
BET	Brunauer Emmet Teller
BSA	Bovine Serum Albumin
CLP	Classification, Labelling and Packaging Regulation
Cr	Chromium
D	Diameter
DPAdCSV	Differential Pulse Adsorptive Cathodic Stripping Voltammetry
DTPA	Diethylene Triamine Pentaacetate
EBSD	Electron Backscatter Diffraction
EDS	Energy Dispersive Spectroscopy
EHEDG	European Hygienic Engineering & Design Group
EU	European Union
Fe	Iron
(FEG) – SEM	Field Emission Gun - Scanning Electron Microscopy
GA	Gas Atomized
GF – AAS	Graphite Furnace - Atomic Absorption Spectroscopy
GHS	Globally Harmonized System for Classification and Labelling of Chemicals
H	Height
JESS	Joint Expert Speciation System
LALLS	Low Angle Laser Light Scattering
LOD	Limit of Detection
LSZ	Lysozyme
Mn	Manganese
Mo	Molybdenum

Ni	Nickel
OCP	Open Circuit Potential
PBS	Phosphate Buffered Saline
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SRL	Specific Release Limit
XPS	X-ray Photoelectron Spectroscopy

Table of contents

Abstract	v
Sammanfattning	vi
List of appended papers	vii
Papers and reports not included in the thesis	viii
Conference presentations based on this thesis	ix
Author's contributions to the appended papers.....	x
Acknowledgements	xi
Abbreviations	xiv
Table of contents.....	xvi
1 Introduction	1
1.1 Motivation and objectives.....	1
2 Background.....	5
2.1 Stainless steel: background and classifications.....	5
2.1.1 Ferritic stainless steels	6
2.1.2 Austenitic stainless steels	6
2.1.3 Duplex stainless steels	7
2.1.4 Martensitic stainless steels	7
2.2 Risk assessment of stainless steels in food contact	8
2.3 Metal release mechanisms of stainless steels	10
2.4 Citric acid – stainless steel interactions	12
3 Experimental.....	15
3.1 Materials	16
3.2 Solutions and exposure parameters	18
3.3 Exposure procedure	21

4	Techniques	23
4.1	GF-AAS	24
4.2	XPS	24
4.3	OCP	25
4.4	Dynamic Polarization	25
4.5	DPAdCSV	26
5	Key Results and Discussions.....	27
5.1	All investigated stainless steel grades passed the compliance test stipulated in the CoE protocol	27
5.2	Surface passivation and chromium enrichment of the outermost surface oxide	28
5.3	Solution and metal composition play an important role even for passive surfaces.....	29
5.4	The surface finish has a considerable effect on the metal release behaviour of stainless steels.....	32
5.5	The outcome of the compliance test strongly depends on the application-specific surface area to solution volume ratio	34
5.6	Repeated exposure of stainless steel to citric acid results in strongly reduced released amounts of metals.....	36
5.7	In-depth investigation of possible metal release mechanisms induced by citric acid	37
5.7.1	Complexation-induced metal release in citric acid: importance of surface and/or solution complexation	40
6	Conclusions.....	43
7	Future work	45
8	References	47

1 Introduction

1.1 Motivation and objectives

Knowledge on the metal release behaviour of stainless steels used in food processing applications and cooking utensils is essential within the framework of human health risk assessment. According to the European regulations such as REACH, GHS and CLP, stainless steel and other alloys are defined as special mixtures of substances [1-3]. However, the fact that these alloys have totally different intrinsic properties compared with their corresponding alloying constituents (e.g. pure Fe, Cr, Mn or Ni) results in the need of cross-reading and new testing for alloys.

Recently, a new European test guideline (here referred as the “CoE protocol”) [4] has been implemented to ensure food safety of metals and alloys, such as stainless steels. This guideline suggests 5 gL⁻¹ citric acid of pH 2.4 as a food simulant for acidic foods. So far, limited assessments exist that investigate the correlation between stainless steel surface characteristics and their metal release behaviour for food application tests using citric acid.

Thus, the primary aims of my PhD studies have been to:

- i)* quantify the extent of metal release from different austenitic, ferritic, and duplex stainless steels exposed into different metal complexing and non – complexing test solutions
- ii)* provide an in-depth understanding of corrosion, surface changes and metal release mechanisms in the presence of metal complex-forming agents (in particular in the presence of citric acid)
- iii)* investigate whether or not the manganese content of certain types of stainless steel can influence the oxidation state of chromium

- iv) elucidate the combined effect of high chloride concentrations and citric acid on the extent of metal release from stainless steel with and without prior surface passivation by citric acid, and
- v) evaluate the effect of key experimental parameters [e.g. surface finish, pH, temperature, buffering and metal complexation capacity, surface area to solution volume ratio (loading), time, citric acid concentration and repeated usage] on the metal release process and concomitant changes of the passive oxide.

These studies apply a fundamental multi-analytical and interdisciplinary approach, schematically shown in Figure 1.

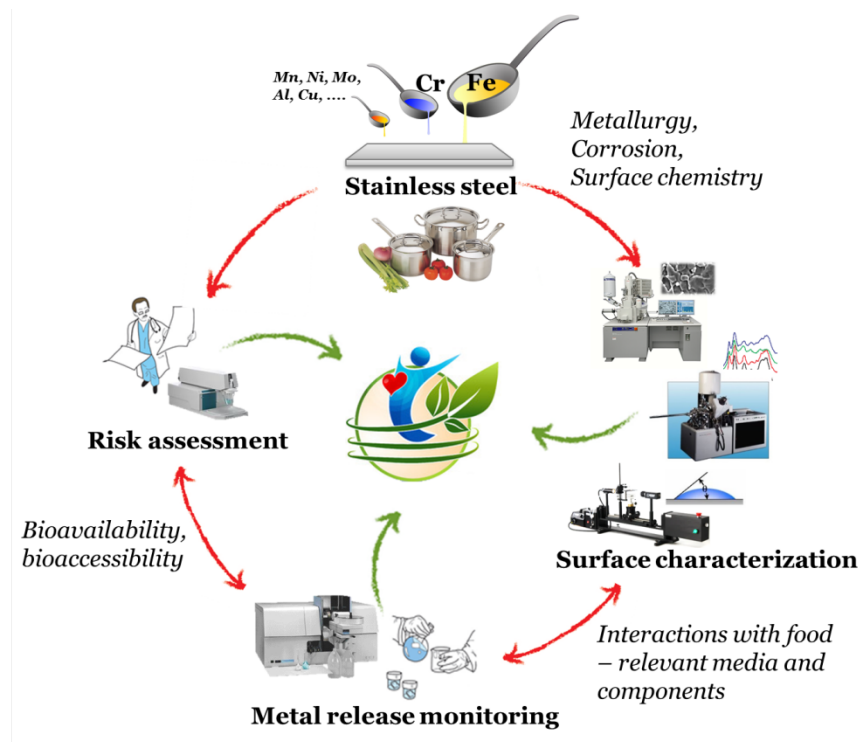


Figure 1: An overall strategy to assess the extent of corrosion and metal release from stainless steels in food contact

The obtained data is expected to be used as a knowledge base within the framework of risk assessment of using different grades of stainless steels in food contact, or after passivation or cleaning of stainless steel with citric acid. Due to the high use of citric acid in environments in which stainless steel has major applications, this type of knowledge is of importance both for relevant industries and end users.

2 Background

2.1 Stainless steel: background and classifications

Stainless steel is a remarkable achievement of modern metallurgy and was discovered when the identification of chromium as an element began [5]. Stainless steel is an iron based alloy with a minimum of 11 wt% chromium [6], which can also have several other alloying elements such as nickel, molybdenum and manganese [7]. Due to the high corrosion resistance of stainless steels in combination with their good mechanical properties, they are used in a wide range of applications, e.g. food and beverage relevant applications, building and construction, biomedical applications and jewellery [4, 8-17].

The corrosion resistance of stainless steels is due to the presence of a very thin self-healing chromium-rich passive surface oxide, with 1 – 3 nm thickness [18-20]. This surface oxide (schematically shown in Figure 2) is believed to contain two layers: *i*) an inner layer, predominantly containing iron and chromium oxides, and *ii*) an outermost layer containing chromium hydroxides and/or oxyhydroxides [18, 21-24].

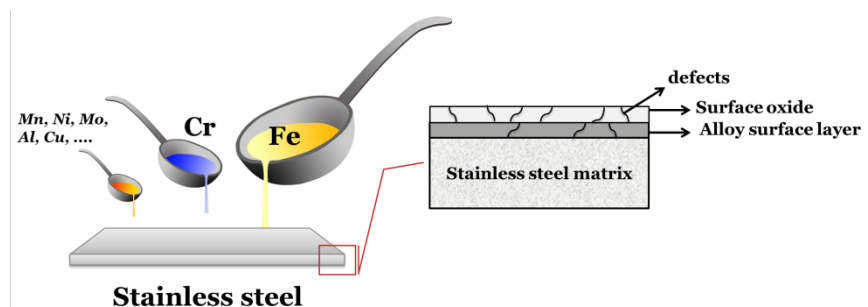


Figure 2: Schematic illustration of stainless steel and its outermost surface oxide, inspired by G. Herting [11]

However, depending on the environmental conditions, oxides of manganese and molybdenum can also be present in the surface oxide of some stainless steel grades (Papers II-III and [18, 20, 23, 25, 26]). In this thesis, the term of “passive film / layer” represents the surface oxide.

Just beneath the passive layer, in the alloy surface layer (schematically shown in Figure 2), nickel, iron and other alloying elements such molybdenum and manganese are enriched [18, 24, 25, 27-30]. Therefore, the presence of defects in the passive film, which can vary depending on the environment and with time [18, 20, 22, 30, 31], can facilitate the release of these metals into different media.

Based on the alloying constituents and microstructure of stainless steels, they are graded into four categories by the AISI system: ferritic, austenitic, duplex and martensitic [7, 11], which are briefly discussed below.

2.1.1 Ferritic stainless steels

Ferritic stainless steels (designated as 400 series by AISI [7]) are nickel free materials with a 10.5 – 30 wt% chromium content and typically used in domestic appliances, kitchenware, containers, building and construction [9, 10]. The absence of nickel makes these grades a more attractive and cost optimized option [10].

2.1.2 Austenitic stainless steels

Austenitic stainless steel grades, with a minimum of 16 wt% chromium, are classified as 200 (Fe – Cr – Ni – Mn – N stainless steels with ≥ 2 wt% Mn) and 300 series (Fe – Cr – Ni stainless steels with ≤ 2 wt% Mn) by AISI [7]. They are the most common grades of stainless steel and typically used in a wide range of applications such as cutleries, kitchen utensils, transport equipment, jewellery, surgical equipment and as implants [4, 11, 13-16]. Since 2000, the 200 series has become more popular in food contact applications, where manganese (up to 8 wt%), often

in combination with nitrogen and copper, have been replaced for nickel. In addition, some non – standardized “new 200 series”, with reduced chromium content of ≤ 15 wt% and nickel content of ≤ 1 wt%, have found an increasing usage in food contact application in Southeast Asia. However, fundamental knowledge of their corrosion and metal release behaviour faces significant knowledge gaps [32].

2.1.3 Duplex stainless steels

Duplex stainless steels have a mixed structure of austenite and ferrite and typically contain chromium (20 – 25 wt%) and nickel (1.5 – 7 wt%) as the main alloying elements [9, 11, 32]. Depending on their application, other alloying elements such as molybdenum, and nitrogen may be added to obtain certain corrosion resistance characteristics [9, 33]. They are commonly used in e.g. bridges, storage tanks and water heaters [33].

2.1.4 Martensitic stainless steels

Martensitic stainless steels (designated as 400 series by AISI [7]) are essentially alloys of chromium (10.5 – 18 wt%) and carbon (0.1 – 1.2 wt%) and typically used in cutlery and knife applications due to their hardness [7, 11]. These grades usually show lower corrosion resistance in comparison with other stainless steel grades, particularly in oxidizing environments [9, 32].

2.2 Risk assessment of stainless steels in food contact

Metals (as ions, complexes, or particles) can if released in certain quantities from stainless steels in food contact affect the organoleptic properties of the food or pose a risk for the end users [4]. Table 1 summarizes the classification of the investigated alloying constituents of this thesis plus their corresponding safe daily intake levels and the SRL values defined by the CoE protocol [4].

Table 1: Classification of the investigated alloying elements of stainless steel, their corresponding safe upper intake levels (for an adult with an average body weight of 60 kg consuming 1 kg/day foodstuffs) in comparison with food examples, and their corresponding SRL values stipulated by the CoE protocol.

Element	Essential trace element for humans	Safe upper daily intake (mg)	Safe upper daily intake of this metal is equal to:	SRL (mg/kg food) [4]
Fe	YES [34, 35]	10 – 15 [36]	100 gr of chicken liver [37]	40
Cr		0.25 [38, 39]	2 kg of turkey ham [40]	0.25
Mn		1 – 10 [41]	100 gr of hazelnuts [37]	1.8
Mo		0.6 [42]	50 gr of lentil [43]	0.12
Ni	NO [44]	0.7 [45]	85 gr of cocoa [35]	0.14

Different restrictions and regulations have been implemented to ensure the safety and suitability of articles of metals and alloys in food contact [4, 46, 47], of which the CoE protocol [4] is the latest technical test guideline implemented by the European Union (EU). The main differences between the CoE protocol [4] and the earlier regulations, such as the Italian Ministerial Decree of 21 March 1973 [46], are: *i*) the use of 5 gL⁻¹ citric acid (pH 2.4) as food

simulant instead of 31.5 gL^{-1} acetic acid (pH 2.4), *ii*) more degrees of freedom in the test setup to enable more application-realistic examinations and *iii*) the stipulation of specific maximum metal release limits (SRL values) into the test medium for each alloying constituent (by considering available toxicological, daily intake, and/or sensitization information [36, 38, 39, 41, 42, 45]) to assess their compliance. The main experimental procedures of the CoE protocol are summarized in Figure 3.

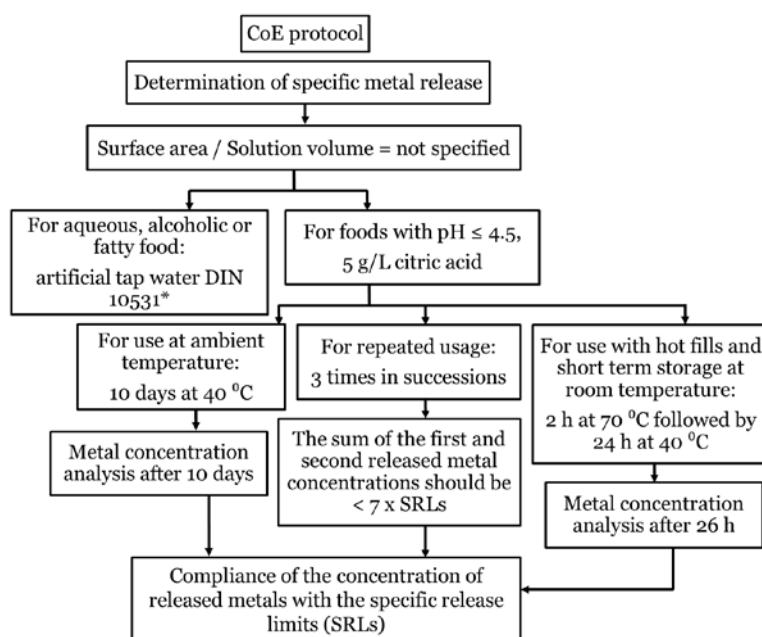


Figure 3: Schematic of the main analytical procedures in the CoE protocol [4].

In the following sections, the metal release mechanisms, key factors affecting the metal release process, and the effect of citric acid on the metal release behaviour of stainless steels are introduced.

2.3 Metal release mechanisms of stainless steels

Metal release mechanisms for stainless steel can be classified as: *i)* electrochemical corrosion, *ii)* chemical or electrochemical dissolution of the surface oxide, or *iii)* physical processes (schematically illustrated in Figure 4). Typically, more than one mechanism occurs at the same time for a stainless steel exposed in a food / biological environment. In addition, due to the continuous changes in the surface oxide of stainless steel and the environmental conditions, the dominance of the mechanisms can change by time [48].

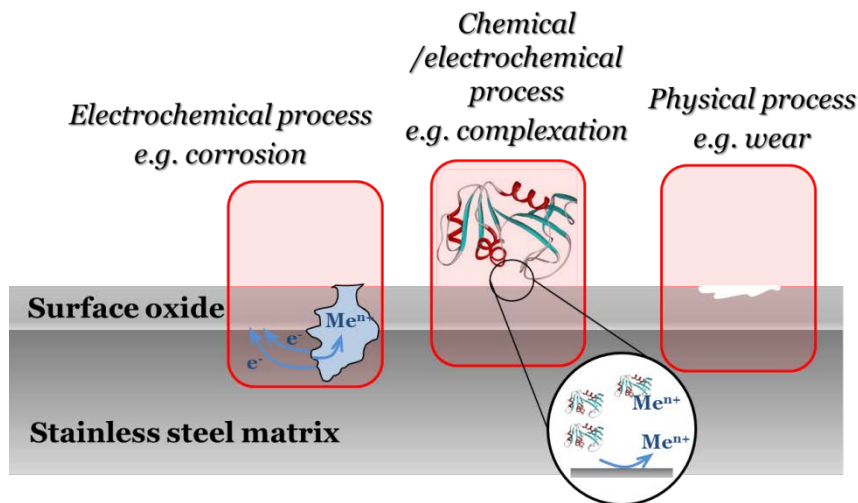


Figure 4: Schematic illustration of metal release mechanisms for stainless steels exposed into a food / biological environment, inspired by [49].

The amount of released metals from stainless steel depends on many factors, summarized in Table 2. It should be noted that, due to the high corrosion resistance and the continuous adjustment of the passive surface oxide of stainless steels, the extent of released metals (Fe, Cr, Ni, Mn, or Mo in this thesis) from these alloys are

generally very low. However, an erroneous usage or grade selection of stainless steels for a certain application can cause active corrosion and result in a significant increase of metal release [48, 50-53].

Table 2: Summary of key factors influencing the metal release behaviour of stainless steels in food applications

Important factors	How can they affect the metal release process of stainless steel?	References
Grade	Total amount of released metals decreases with increased the Cr bulk content of stainless steel, except for non-aggressive solutions. However, no direct correlation exists between the Cr bulk content and the amount of released individual alloying elements	[12, 26, 48, 54, 55] and Papers I-III
Surface finish	Increased metal release for abraded surfaces in comparison with aged or as – received surface finishes	[11, 53, 56-59] and Papers I-II
Presence of organic ligands, phosphate and/or proteins	May either increase ligand-induced dissolution by enhancing the metal complexation capacity of the solution or block surface sites that retards dissolution and metal release	[17, 31, 60-71] and Paper I
Buffering capacity of solution	Increased metal release with increased buffering capacity at acidic pH	[72] and Paper I
Loading (surface area to solution volume ratio)	Increased loading results in enhanced metal release in solution	[73-76] and Paper II
Pre-usage	Repeated use of stainless steel commonly results in reduced amounts of released metals	[74, 77-80] and Papers II-III

Table 2 Cont.		
Important factors	How can they affect the metal release process of stainless steel?	References
pH	Changes the <ul style="list-style-type: none"> - charge of the surface (hydr)oxide - ligand conformation and their adsorption behaviour - ionic strength - degree of protein aggregation - nearly all corrosion and dissolution processes 	[48, 60, 64, 68, 81-83] and Papers III-IV
Temperature	An increased temperature can: <ul style="list-style-type: none"> - significantly enhance metal release - alter the surface oxide properties and increase stainless steel tendency towards pitting - substantially enhance the stability of formed metal complexes - enhance passivation processes and in some cases result in lower subsequent metal release 	[7, 51, 84, 85] and Paper II
Exposure time	<ul style="list-style-type: none"> - Increase in passivity with time that can strongly reduce the amount of released metals - In environments of high risk for pitting (e.g. high chloride): increased probability of pitting events and stabilization of pits 	[11, 14, 55, 56, 59, 86-90] and Papers I-III

2.4 Citric acid – stainless steel interactions

Interactions between citric acid and stainless steel are of high importance for food contact risk assessments [4], surface cleaning [91], and surface passivation [79, 92]. Citric acid (as a tricarboxylic acid with pK_a values of 3.1, 4.8 and 6.4 [93]) is a strongly metal

complexing agent. It can form different complexes with metals present both in solution (solution complexation) and in the surface oxide (surface complexation). Depending on the strength of the formed complexes and the adjacent bonds, which can vary by changes in pH and temperature [60, 84], the formed complexes may detach from the surface and enhance the amount of released metals.

The metal release behaviour of different grades of stainless steel (with different surface finishes) exposed to citric acid containing solutions (with different concentrations and/or pH values) has recently been investigated (Papers II-IV, technical report VIII and [94]), as citric acid is one of the suggested test solutions of acid food in the newly implemented European test guideline (the CoE protocol) [4]. The results suggest that the release of alloying constituents from stainless steel into citric acid containing solutions (with a preferential Fe release) is mostly governed by the chemical and/or electrochemical oxide dissolution (e.g. protonation, reductive or oxidative dissolution or complexation – induced dissolution) [31, 48, 95] and that usually no active corrosion occurs (Papers II-III).

A combined metal release and surface wettability study of polished stainless steel grade AISI 304 in 5 gL⁻¹ citric acid solution suggested a time-dependent adsorption-controlled ligand-induced metal release mechanism, Figure 5 [31]. However, it should be noted that this study was carried out at pH 2.4, where metal-citrate complexation is of minor importance in comparison to protonation effects, except for chromium species, for which both protonation and complexation play an important role independent of the pH (Paper V and [48]). Metal release studies of abraded stainless steel grade 304 (1200 SiC, 24 h aged/stored at room temperature and low humidity) into 5 gL⁻¹ citric acid solution of pH 4.8 suggest that the adsorption of citric acid occurs faster at this pH when compared to pH 2.4. This is because the metal release rapidly enhances during the first hour of exposure, but

does not increase further up to 24 h at pH 4.8 (except for Cr), Paper V.

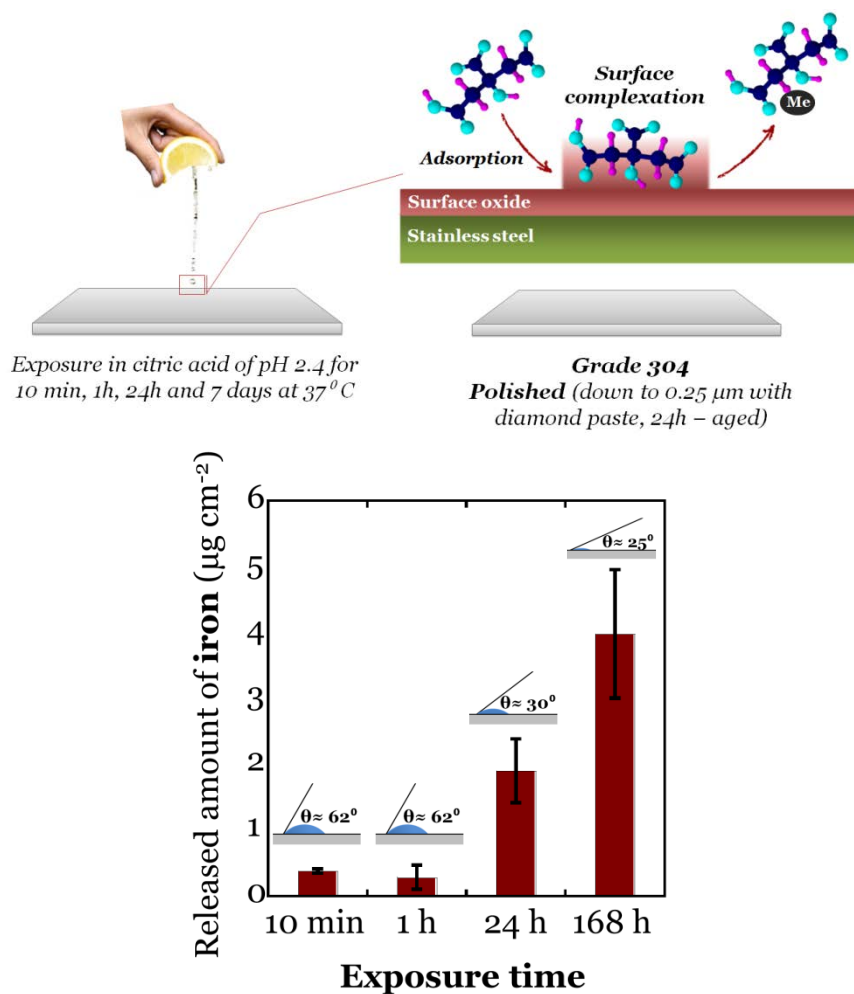


Figure 5: Changes in the released amount of Fe from grade 304 stainless steel and the measured contact angle versus exposure time into 5 gL^{-1} citric acid. Data from [31]

3 Experimental

The described work in this thesis was all performed under laboratory conditions. A multidisciplinary approach was employed to link the metal release behaviour to surface properties of different stainless steel grades after exposure into different metal complexing and non – complexing test solutions.

The information regarding the investigated stainless steel grades, their corresponding microstructure, bulk nominal composition, and the investigated surface finishes are summarized in Table 3.

Table 4 illustrates the summary of all investigated test solutions, their corresponding composition, and the exposure parameters (consisting the pH, temperature and exposure time) (Papers I –V).

Triplicate samples and one blank sample (solution without any metal coupon) were exposed in parallel for each investigated material, time period, solution, pH, and temperature. Schematic illustration of the exposure procedure for metal release and surface oxide investigations is shown in Table 5.

Detailed information on all experimental information, equipment, cleaning procedures, exposure conditions and instruments (e.g. furnaces) is given in the respective papers.

3.1 Materials

Table 3: Investigated stainless steel massive grades (composition in weight-%) and surface preparation, based on supplier information (Papers I – V). Stainless steel powders of Paper I are not discussed / included in this thesis.

Name (in this thesis)	UNS (ASTM)	EN	Surface finish	Cr wt%	Mn wt%	Ni wt%	Mo wt%	C wt%	S wt%	Papers
EN1.4003	S40977	1.4003	2B	11	1	<1	-	-	-	III
430	S43000	1.4016	2B	16	0.3	0.1	0.02	0.03	0.002	III
430	S43000	1.4016	A	16.0	0.5	0.2	0.06	0.04	0.002	I
204	S20431 (+Cu)	1.4597 (+Cu)	2B	16	9.1	1.1	0.2	0.1	0.004	III
201	S20100	1.4372	2D, A	16.9	5.8	3.6	0.2	0.11	0.002	II, III
316L	S31603	1.4404	2B, A [56]	16.6	1.0	10.6	2.1	0.03	0.001	I
316L	S31603	1.4404	2B, SB, N4, SSW, A	17	1.3	10.2	2.0	0.02	-	III, IV
304	S30400	1.4301	2B, SB, N4, SSW, PP, A	17.9	1.2	9.0	0.4	0.04	0.003	III – V
304	S30400	1.4301	A, 2B, 2D, BA (2R)	18.1	1.1	9.0	0.3	0.05	0.002	I, [58]
310	S31000	1.4841	A	24.2	0.9	19.1	0.2	0.06	0.001	I
LDX 2101	S32101	1.4162	2B	21.4	4.8	1.6	0.3	0.02	0.001	III

Table 3 Cont.

Name (in this thesis)	UNS (ASTM)	EN	Surface finish	Cr wt%	Mn wt%	Ni wt%	Mo wt%	C wt%	S wt%	Papers
2205	S32205	1.4462	A	22.5	1.7	5.6	3.1	0.02	0.001	I

☐ ferritic microstructure
 ☐ austenitic microstructure
 ☐ duplex microstructure

2B: bright cold rolled, annealed, pickled, and skin-passed;

2D: dull cold rolled, annealed and pickled;

SB: abraded using a Scotch-Brite brush;

N4: polished with a 220 grit grinding belt;

BA (2R): cold rolled and bright annealed;

A: ground (abraded) by 1200 grit SiC;

SSW: abraded by commercially available Stainless Steel Wool, "fixa stålboll", Sweden;

PP: pre-passivated in 5 gL⁻¹ citric acid (pH 2.4) at 70 °C for 2 h;

NA: no data available

All coupons were edge ground by 1200 grit SiC, 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).

3.2 Solutions and exposure parameters

Table 4: Summary of the test solutions and exposure parameters (Papers I –V)

Name (in this thesis)	Composition	pH	Temperature / exposure time	Papers
PBS	8.77 gL ⁻¹ NaCl + 1.28 gL ⁻¹ Na ₂ HPO ₄ + 1.36 gL ⁻¹ KH ₂ PO ₄	7.4	37 °C (2 h, 4 h, 8 h,) 24 h (1 day); 168 h (1 week)	I
PBS + BSA	8.77 gL ⁻¹ NaCl + 1.28 gL ⁻¹ Na ₂ HPO ₄ + 1.36 gL ⁻¹ KH ₂ PO ₄ + 10 gL ⁻¹ BSA			
PBS + LSZ	8.77 gL ⁻¹ NaCl + 1.28 gL ⁻¹ Na ₂ HPO ₄ + 1.36 gL ⁻¹ KH ₂ PO ₄ + 2.2 gL ⁻¹ LSZ			
Na₂HPO₄	8.84 gL ⁻¹ Na ₂ HPO ₄ ·2H ₂ O	4.5		
ALF [56, 96]	0.05 gL ⁻¹ MgCl ₂ + 3.21 gL ⁻¹ NaCl + 0.07 gL ⁻¹ Na ₂ HPO ₄ + 0.04 gL ⁻¹ Na ₂ SO ₄ + 0.13 gL ⁻¹ CaCl ₂ ·H ₂ O + 6.00 gL ⁻¹ NaOH + 20.8 gL ⁻¹ C ₆ H ₈ O ₇ (citric acid)+ 0.06 gL ⁻¹ H ₂ NCH ₂ COOH + 0.08 gL ⁻¹ C ₆ H ₅ Na ₃ O ₇ ·2H ₂ O + 0.09 gL ⁻¹ C ₄ H ₄ O ₆ Na ₂ ·2H ₂ O + 0.09 gL ⁻¹ C ₃ H ₅ NaO ₃ + 0.09 gL ⁻¹ C ₃ H ₃ O ₃ Na	4.5		
CA	5 gL ⁻¹ citric acid (0.3 vol%)	2.4	40 °C, 70 °C, 100 °C 3 x 30 min, 2 h, 26 h, 240 h (10 days)	II
			70/40 °C * 6 x 30 min, 2 h, 26 h, 240 h (10 days)	III

Table 4 Cont.

Name (in this thesis)	Composition	pH	Temperature / exposure time	Papers
OCA	7.8 gL ⁻¹ acetic acid + 1.84 gL ⁻¹ NaOH	4.5	40 °C 24 h	II
0.01CA	0.01 gL ⁻¹ citric acid + 7.7 gL ⁻¹ acetic acid + 1.83 gL ⁻¹ NaOH			
0.1CA	0.1 gL ⁻¹ citric acid + 7.7 gL ⁻¹ acetic acid + 1.85 gL ⁻¹ NaOH			
5CA	5 gL ⁻¹ citric acid + 6.2 gL ⁻¹ acetic acid + 2.84 gL ⁻¹ NaOH			
20.8CA	20.8 gL ⁻¹ citric acid + 4.21 gL ⁻¹ NaOH			
AA	31.5 gL ⁻¹ acetic acid (3 vol%)	2.4	40 °C, 100 °C 240 h (10 days)	II
Artificial tap water [97]	0.12 gL ⁻¹ NaHCO ₃ + 0.07 gL ⁻¹ MgSO ₄ ·7H ₂ O + 0.12 gL ⁻¹ CaCl ₂ ·2H ₂ O	7.5	70/40 °C 2 h, 26 h, 240 h (10 days)	III
NaCl	29.22 gL ⁻¹ NaCl (0.5 M), pH 2.2 was adjusted by 65% ultrapure HNO ₃	2.2, 5.5	70/40 °C	
NaCl + CA	29.22 gL ⁻¹ NaCl + 5 gL ⁻¹ citric acid, pH 5.5 was adjusted with 50% NaOH	2.2, 5.5	26 h	
3.1CA	5 gL ⁻¹ citric acid + 850 µgL ⁻¹ 50% NaOH	3.1	70/40 °C 26 h	IV

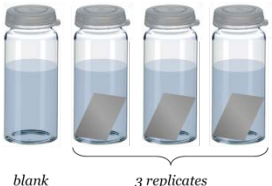
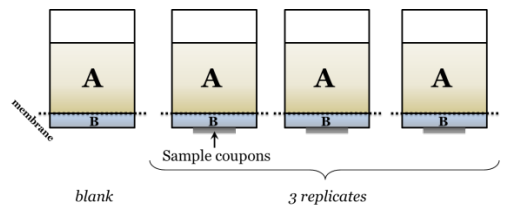
Table 4 Cont.

Name (in this thesis)	Composition	pH	Temperature / exposure time	Papers
4.8CA	5 gL ⁻¹ citric acid + 2980 µgL ⁻¹ 50% NaOH	4.8	70/40 °C 26 h	IV
			40 °C 30 min, 1 h, 2h	V
6.4CA	5 gL ⁻¹ citric acid + 4280 µgL ⁻¹ 50% NaOH	6.4	70/40 °C	IV
11CA	5 gL ⁻¹ citric acid + 4550 µgL ⁻¹ 50% NaOH	11	26 h	
KNO₃	1.01 gL ⁻¹ KNO ₃ (0.01 M)	3.1, 4.8, 6.4	40 °C 24 h	V
CA + KNO₃	5 gL ⁻¹ citric acid (0.026 M) + 1.01 gL ⁻¹ KNO ₃			
PAA + KNO₃	16.1 gL ⁻¹ 35 wt% polyacrylic acid (0.078 M) + 1.01 gL ⁻¹ KNO ₃			
5 ppm Fe KNO₃	5 ppm Fe + 1.01 gL ⁻¹ KNO ₃			

* 70/40 °C means the first 2 h at 70 °C followed by 40 °C (for 0 h, 24 h or 238 h to simulate cooling of food and for short and long term applications)

3.3 Exposure procedure

Table 5: Schematic illustration of the exposure procedure for metal release and outermost surface oxide investigations presented in this thesis

Exposure procedure	Exposed surface area / volume of test solution ($\text{cm}^2 \text{ mL}^{-1}$)	Papers
 <p>blank</p> <p>3 replicates</p> <p><i>Clear glass with snap-cap</i></p>	$6 \text{ cm}^2 / 6 \text{ mL} = \mathbf{1}$	I - V
	$(6 \text{ cm}^2 / 24 \text{ mL} = \mathbf{0.25})$, $(6 \text{ cm}^2 / 12 \text{ mL} = \mathbf{0.5})$, $(6 \text{ cm}^2 / 8 \text{ mL} = \mathbf{0.75})$, $(6 \text{ cm}^2 / 4.7 \text{ mL} = \mathbf{1.3})$, $(6 \text{ cm}^2 / 3 \text{ mL} = \mathbf{2})$	II
 <p>membrane</p> <p>A</p> <p>B</p> <p>Sample coupons</p> <p>blank</p> <p>3 replicates</p> <p><i>Solution A: KNO_3, CA + KNO_3 or PAA + KNO_3 (5 mL, pH 3.1, 4.8, 6.4)</i> <i>Solution B: KNO_3 (1 mL, pH 3.1, 4.8, 6.4)</i></p> <p><i>Special designed plexiglas cells</i></p>	$\pi \text{ cm}^2 / 6 \text{ mL} \approx \mathbf{0.5}$	V

4 Techniques

Several complementary analytical techniques (presented in Table 6) have been employed in order to provide an in-depth understanding of surface changes, metal release processes and possible corrosion mechanisms of different grades of stainless steels when in contact with food simulants.

Details of all analytical methods are given in the respective papers. Information on selected techniques, indicated in Table 6, is briefly given in sections 4.1 – 4.5.

Table 6: Summary of employed techniques in Papers I – V

Technique	Used to investigate:	Papers
GF-AAS	bioaccessibility (metal release)	I - V
XPS	outermost surface oxide chemical and elemental composition	I - V
OCP	corrosion studies	II, III
Dynamic Polarization		III
DPAdCSV	aspects of bioavailability (chromium speciation)	II
EBSD	crystallographic structure	III
(FEG)-SEM	surface morphology	I
BET	specific surface area	I
LALLS	Particle size distribution	I

 *Not discussed in the thesis*

4.1 GF-AAS

The concentration of released, non-precipitated, metals from different grades of stainless steels after exposure into different test solutions was determined for acidified samples ($\text{pH} < 2$) by means of GF-AAS. GF-AAS is a principal tool in analytical chemistry due to its high sensitivity to distinguish different elements of a complex sample solution [98], with a LOD of typically below $1 \mu\text{gL}^{-1}$. This technique works based on the capacity of an atom to absorb very specific wavelengths of light [99]. In this method (schematically shown in Figure 6), a substance is decomposed into atoms in a graphite furnace and then the quantity of each element is measured by absorption of light from the gaseous atoms by considering Beer's Law [98, 99]. Detailed information of this method is given in Papers I – V.

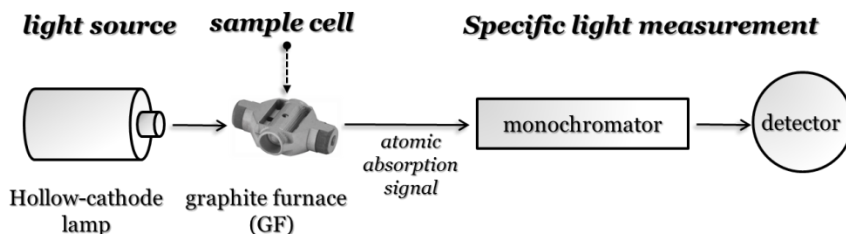


Figure 6: Schematic illustration of GF-AAS components [98, 99]

4.2 XPS

Compositional analysis of the outermost surface oxide of different stainless steel grades (with the information depth of a few nanometers [19, 20]) before and after exposures were performed by XPS. XPS is one of the most commonly used non-destructive surface analysis techniques that enables mapping of elements and of chemical states. In XPS, the surface of a sample is irradiated with photons of characteristic energy, which interact with core electrons of the sample atoms, create ionized states and lead to

photoelectron emission [100]. XPS of this study was performed using an instrument equipped with an Al K_{α} radiation source, with the X-ray photon energy of 1486.6 eV [100]. More details are given in Papers I – V.

4.3 OCP

In order to monitor metal release processes of different stainless steel grades during exposure into different test solutions / conditions and investigate possible corrosion mechanisms (which can largely influence the amount of released metals), OCP analysis was performed. OCP is the potential of a working electrode (metal sample) with respect to a reference electrode (e.g. Ag/AgCl) when no current flows to or from it [101]. By measuring changes in OCP of metal samples over time in different test solutions, useful information about the corrosion and/or passivation behaviour of metals can be provided. In this thesis (Papers II – III), the OCP analysis was carried out in order to investigate the corrosion behaviour of different stainless steel grades in simulated food media and to clarify possible contribution of corrosion processes to the metal release from different stainless steel grades. More details and experimental set-ups can be found in Papers II – III.

4.4 Dynamic Polarization

Dynamic polarization measurements were conducted to investigate the corrosion resistance of different stainless steel grades in simulated food media (Paper III). In this method, a three electrode electrochemical cell was used, which contains a working electrode (metal sample), a reference electrode (Ag/AgCl) and a counter electrode (Pt wire). During polarization, the potential was anodically swept (starting from the OCP with a scanning rate of 0.0005 Vs⁻¹). For chloride free solutions, the backward scan thereafter started at around 1.3 V (the potential at which oxygen

evolution occurs at pH 2.4) and stopped at the starting potential (which was the initial OCP potential of the corresponding grade and solution). More details are given in Paper III.

4.5 DPAdCSV

DPAdCSV analysis was carried out to speciate the oxidation state of released Cr from stainless steel grades after exposure into food simulants stipulated in the CoE protocol [4]. This method is based on the time-dependent reaction of Cr species in a supporting electrolyte that contains the complex forming agent of DTPA, the catalytic oxidant of NaNO_3 and NaCH_3COO as a buffer agent, which are known as the most useful agents for the analysis of trace levels of Cr and its speciation using stripping voltammetry [102, 103]. During the measurements, the pH was kept constant at 6.2 ± 0.1 , since at the pH of around 6 and under these electrochemical conditions, Cr(VI) does not form complexes with DTPA and hence can be determined. [103]. Information about the experimental set-up and parameters can be found in Paper II.

5 Key Results and Discussions

This chapter provides a selection of results and discussions chosen from Papers I – V, the literature survey findings, the technical reports VII – VIII, the conference contributions IX – XIII, and some unpublished data.

5.1 All investigated stainless steel grades passed the compliance test stipulated in the CoE protocol

The released amount of metals [Fe, Cr, Mn, Ni, and Mo (only measured for grade 316L)] from all stainless steel grades investigated was below the SRL values stipulated in the CoE protocol [4], in both citric acid and artificial tap water solutions (Table 7, summary of maximum amounts of released metals and their comparison to the SRLs). In the case of non-complex forming test solution of artificial tap water, released amounts of metals were significantly below the findings in citric acid and were close to the LOD of GF-AAS (Papers II – III, technical reports VII – VIII).

Table 7: Summary of maximum released amounts of metals from their corresponding investigated stainless steel grades during 0 – 240 h at 70 °C (first 2 h) followed by 40 °C in citric acid (pH 2.4) compared with the SRLs. The surface area to solution volume ratio (loading) was 1 cm²mL⁻¹.

	Fe	Cr	Ni	Mn	Mo
SRL	40	0.25	0.14	1.8	0.12
<i>released concentration in (mgL⁻¹)</i>					
EN1.4003	7.0	0.14	<i>not available (NA)</i>		
304	1.6	0.21	0.05	0.02	NA
316L	1.6	0.13	0.06	0.05	0.02
204	2.2	0.18	0.006	0.35	NA

It should be noted that metal release from the investigated as-received stainless steel coupons in citric acid predominantly occurred during the first 2 hours of exposure, followed by considerably reduced release rates. Very low amounts of metals were released into citric acid (pH 2.4) during 10 days of exposure which quantitatively corresponds to an alloy mass loss of less than 0.000025 % with the preferential release of Fe and Mn. No active corrosion was evident at given exposure conditions (Papers II – III, technical reports VII – VIII).

Released Cr from stainless steel grades of 304 (with 2B surface finish) and 201 (with 2D surface finish) was in trivalent form and no hexavalent form was detected either in citric acid (pH 2.4 and pH 4.5) or in artificial tap water (pH 7.5) up to 10 days of exposure (Paper II and technical report VII). These findings are in agreement with previous studies on chromium speciation of released Cr from different chromium containing alloys in a range of different biological simulants [13, 86, 95, 104, 105]. Cr(III) is the thermodynamically expected form of chromium in these conditions [48].

5.2 Surface passivation and chromium enrichment of the outermost surface oxide

All investigated stainless steel surfaces (both the as-received and abraded grades) gained in passivity (enrichment of chromium in the surface oxide) with time upon exposure in citric acid (independent of pH). For example, compared to the bulk chromium content of grade 304 (which is 18 wt%), the surface oxide chromium content was 41 wt% for the as-received surface (2B) due to chromium enrichment. After exposure to citric acid (pH 2.4), the chromium content of the outermost surface oxide of grade 304 further increased (to 48 wt%, 58 wt% and 61 wt% after 2 h, 26 h and 10 days, respectively), mainly due to preferential Fe release, which is well documented at acidic conditions [54-56, 59,

64, 74, 86, 95, 96], Figure 7. (Papers I – V, technical reports VII – VIII, conference contributions IX – XIII).

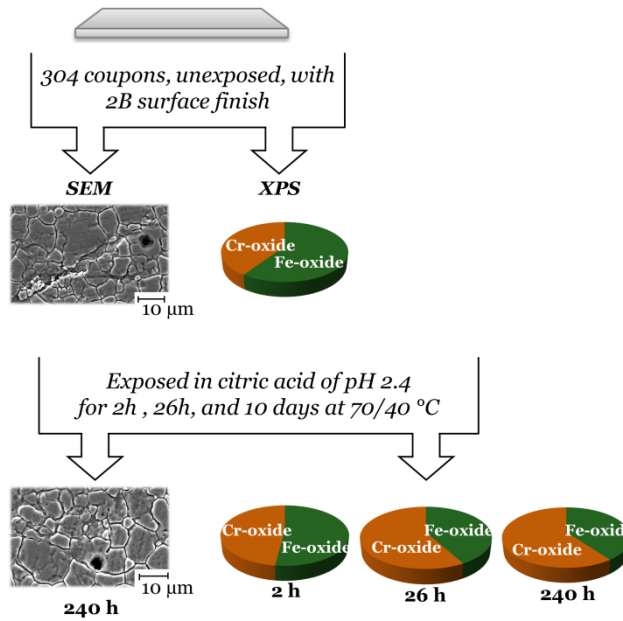


Figure 7: Changes in surface morphology (SEM images) and chromium enrichment of the outermost surface oxide (XPS analysis) of as-received grade 304 after different exposure periods (up to 10 days) in 5 gL⁻¹ citric acid (pH 2.4) for 2 h at 70 °C followed by exposure at 40 °C for another 0, 24, and 238 h.

5.3 Solution and metal composition play an important role even for passive surfaces

Figure 8 indicates the comparison between the total amount of released metals from different investigated stainless steel grades into citric acid (pH 2.4) and artificial tap water (pH 7.5), stipulated in the CoE protocol [4] and in PBS solutions with and without proteins (Papers I – III, technical reports VII – VIII, [54]).

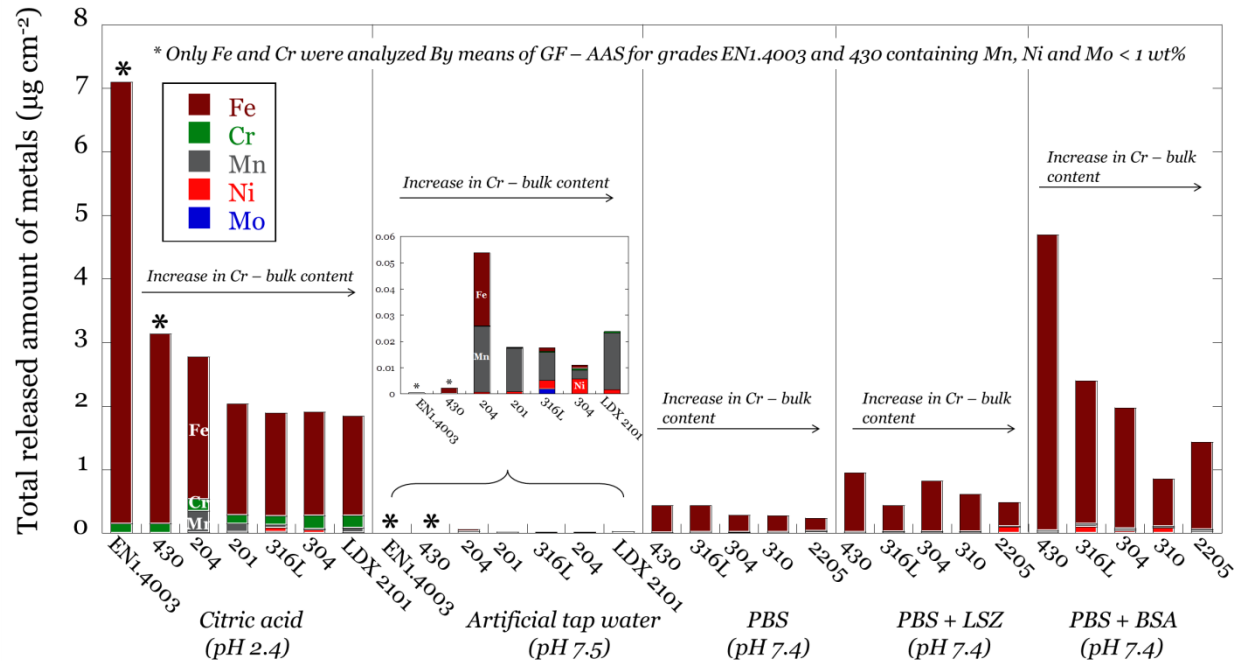


Figure 8: Comparison of the total amount of released metals from different investigated as-received stainless steel grades during 0-240 h at 70 °C (for the first 2 h) followed by 40 °C into 5 gL⁻¹ citric acid (pH 2.4) and artificial tap water (pH 7.5), stipulated in the CoE protocol [4], and abraded (1200 grit SiC) coupons into PBS solutions, with and without LSZ and BSA proteins (pH 7.4) after 1 week (168 h) of exposure (Papers I – III, technical reports VII – VIII, [54])

For all grades, as expected (Paper II, [48]), released amounts of metals were significantly higher in the complex forming solutions of citric acid (pH 2.4) and PBS solutions (pH 7.4) compared with the tap water solution (pH 7.5). It should though be stressed that all released metal concentrations were very low. The total amount of released metals from each grade into citric acid and PBS solutions was dominated by Fe (77 – 98 %) for all grades (Papers I – III, technical reports VII – VIII, [54]), in agreement with literature findings in similar solutions [48, 73, 86, 95].

As can be seen in Figure 8, an increased bulk content of Cr, which generally enhances the corrosion resistance [22], reduce the total amount of released metals, dominated by Fe. However, this trend is not valid for each individual alloying elements (Papers I – III, [48]). Fe (in citric acid and PBS solutions) and Mn (in all test solutions) were preferentially released, as compared to their corresponding bulk content (Papers I – III). In solutions with a pH above 6, the probability of precipitation of Fe and Cr, and to some extent Mn, increases (Paper V, [60]), which may result in lower levels of released metal in solution. Preferential release of Fe and Mn from the stainless steel surface oxide can be partly explained by the higher solubility of Fe- and Mn-oxides compared with Cr-oxides at acidic and neutral pH [69, 70, 106, 107] and can also be due to the absence of Ni in the outermost surface oxide [18, 20, 24, 48, 108].

Compared to pure Fe metal, pure Ni metal and Mn(IV) oxide, the extent of released Fe, Ni and Mn from different grades of stainless steels in the complex forming solutions was lower by far [56, 57, 109-111]. Nevertheless, there were still significant differences in the amount of released metals detectable between the different grades. No active corrosion or stable pitting occurred for the investigated stainless steel grades either in citric acid or in artificial tap water (Papers II – III).

While the test solutions of artificial tap water (pH 7.5) and PBS solutions (pH 7.4) were in a similar pH range, the extent of total released metals in PBS was significantly higher (Figure 8),

especially in the presence of LSZ and BSA proteins. This highlights the importance of the presence of proteins and ligand forming agents, such as phosphate and chloride ions, which are present in PBS. The complexation capacity of these solutions strongly depends on the pH [94, 112] and on the metal release process of stainless steel (Papers I – V, [12, 54, 94, 95, 113, 114]).

5.4 The surface finish has a considerable effect on the metal release behaviour of stainless steels

Surface finish / treatments can noticeably influence the amount of released metals from different stainless steel grades at a given exposure condition (Papers II, III, technical report VII, [56, 58, 59, 74, 77]). In addition, it affects the passive film composition, the surface roughness, wettability, electrochemically active areas and the isoelectric point [58, 74, 115-117].

Figure 9 illustrates the importance of the surface finish on the extent of released metals from two austenitic grades. The highest amount of metals is released into the test solutions of ALF (pH 4.5) and citric acid (pH 2.4) from the surface finishes of abraded (A), with a 2.7-fold increase compared to 2B surface finish, and Scotch-Brite brushed (SB), a 3.7-fold increase. However, while an average surface roughness (R_a) of less than $0.8\text{ }\mu\text{m}$ is specified by the EHEDG and AMI for the food contact materials to ensure their corrosion resistance and cleanability [118], no clear relationship could be observed among the surface roughness of different surface finishes and the extent of released metals (Table 8), in agreement with previous studies [58, 74, 117]. For example, while both the abraded (A) and bright annealed (BA) surfaces finishes had the lowest surface roughness compared to the other investigated surface finishes (Table 8), the extent of released metals from grade 304 reached the maximum value for the A surface finish and the minimum for the BA surface finish at the same exposure condition.

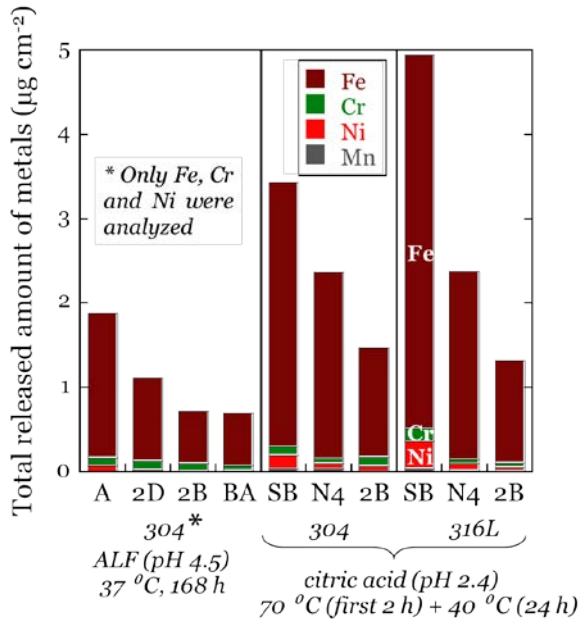


Figure 9: Total amount of released metals from austenitic stainless steel grades of 304 and 316L of different surface finish after exposure into citric acid containing solutions of different pH (Paper III, technical report VII, and [58])

Table 8: Summary of different surface finishes presented in Figure 9, their corresponding R_a values, based on literature findings, and examples of their use in food related application [58, 74, 118-123]

Surface finish	R_a (μm)	Application examples in food contact
BA (2R)	0.03 – 0.2	cookers, cookware, cutlery
A	0.13	not applicable
SB	0.1 – 0.4	not available
2B	0.1 – 0.5	the most commonly used surface finish in food industry, e.g. cutlery, beer kegs, process vessels and tanks
N4	0.8	restaurant and kitchen equipment, food processing
2D	0.2 - 1	beer kegs

The OCP investigation of grade 316L with SB surface finish, with the highest extent of released metals, Figure 9, indicated an increased passivity with time and no active and/or metastable corrosion could be observed (technical report VII). Furthermore, the OCP values obtained for grade 316L with SB surface finish were higher compared to grade 316L with a 2B surface finish, with the lowest extent of released metals at the same exposure conditions (technical report VII). This suggests that the initially more active SB surface could be passivated faster compared with the 2B surface, resulting in higher OCP values and initially a higher extent of metal release. Since no repeated metal release studies were performed for this surface finish, it could not be ruled out whether the metal release of the SB surface would be lower or equal compared to a 2B surface after the initial passivation process.

5.5 The outcome of the compliance test strongly depends on the application-specific surface area to solution volume ratio

Depending on the food contact application, the surface area to solution volume ratio (loading) varies. A higher loading will hence result in a higher concentration of metals in solution, as e.g. shown for Cr in Figure 10. This is in agreement with other findings (Paper II, technical reports VII – VIII, [74, 75]). Since the surface area to solution volume ratio is not clearly specified in the CoE protocol and defined as application-specific [4], it can be speculated that the same material examined at a low ratio may pass the compliance test and stipulated SRL concentrations, while possibly fail if tested at a significantly higher ratio (Paper II).

Therefore, the surface area to solution volume ratio is the single most important factor that affects the outcome of a compliance test with respect to the SRL concentrations.

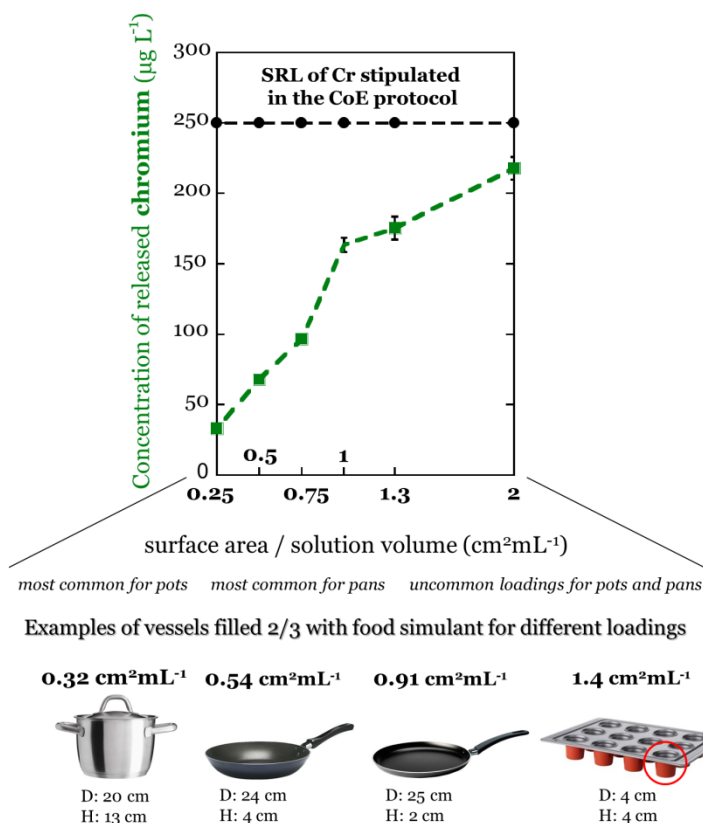


Figure 10: Changes in observed concentrations of Cr compared with the Cr stipulated SRL value in the CoE protocol [4] when increasing the surface area to solution volume ratio (loading) from 0.25 to 0.5, 0.75, 1, 1.3, and 2 $\text{cm}^2\text{mL}^{-1}$ for austenitic stainless steel grade 201 (surface finish A) after 2 h of exposure in citric acid (pH 2.4) at 70 °C (Paper II, technical reports VII – VIII). The example loadings for kitchen utensils are calculated according to the CoE protocol definition of loading: “the total exposed surface area (in contact with $\frac{2}{3}$ volume) / $\frac{2}{3}$ volume”. Example images of different loadings are taken from IKEA webpage (<http://www.ikea.com/se/sv/>).

5.6 Repeated exposure of stainless steel to citric acid results in strongly reduced released amounts of metals

Metal release upon repeated usage of stainless steels in food contact is very important for risk assessment of these alloys. However, most studies only investigate the initial extent of released metals, which is typically higher compared with subsequent exposures [48].

Upon repeated exposure of grades 201, 304 and 316L in citric acid or acetic acid (for three or six subsequent 30 min exposure at 100 °C), the amount of all released metals decreased (about 10-fold) for all grades suggesting enhanced surface passivation at these conditions, Figure 11 (Papers II – III, technical reports VII – VIII).

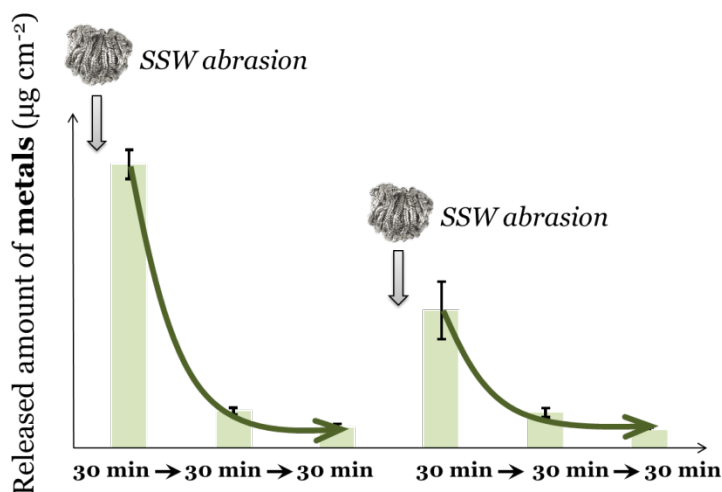


Figure 11: Schematic illustration of released amount of metals (Fe, Cr, Mn and Ni) upon repeated exposure of stainless steel grade 304 for six subsequent 30 min exposure in 5 gL⁻¹ citric acid (pH 2.4) at 100 °C. All samples were abraded by a commercially available Stainless Steel Wool (SSW) before the 1st and 4th exposure in the sequence (Papers II – III, technical reports VII – VIII).

These findings are consistent with other studies carried out on different grades of stainless steels that show reduced metal release and strong chromium enrichment in the surface oxide upon repeated exposures to different food simulants [74, 77-79]. The results show that repeated usage of stainless steel in contact with food commonly results in reduced amounts of released metals and suggests that stainless steel can be generally considered safe to use in contact with food as long as the correct grade is applied. However, it should be noted that an incorrect usage or grade selection for a given application can result in active corrosion [48, 50-52].

5.7 In-depth investigation of possible metal release mechanisms induced by citric acid

The metal release behaviour of different stainless steel grades have been earlier investigated into citric acid containing solutions from a food safety point of view, since citric acid is suggested as one of the food simulants (and the most aggressive one) in the relatively new European test guideline [4] (Papers II – V, technical reports VII – VIII). The results clearly indicate that citric acid induces an initial metal release (that mostly occurs during the first 2 h of exposure) and concomitant surface passivation that hinders further release of alloying elements (Papers II – V, technical reports VII – VIII).

So far, several mechanisms have been suggested for the release of alloying constituents from stainless steels in the presence of complex forming agents such as citric acid (Paper I, [31, 48, 62, 63, 65, 72, 95, 124], of which protonation (at low pH ranges) and adsorption-controlled surface complexation followed by complex detachment (at weakly acidic and neutral pH ranges) are proposed as the predominant metal release mechanisms (Paper V). This is suggested to be the case as long as physical processes (e.g. wear)

do not take place and can be excluded, and that corrosion processes are negligible.

Table 9 provides a schematic illustration of changes in the predomination of the main metal release mechanisms suggested for abraded grade 304 (Paper V). In order to distinguish between the effects of pH (that influences protonation, corrosion processes and dissolution) and complexation on the metal release behaviour of different investigated alloying elements (Fe, Cr, Mn and Ni), non-complexing test solution of KNO_3 (KNO_3) and citric acid containing KNO_3 solution (CA + KNO_3) of varying pH (chosen based on the pK_a values of citric acid) were used (Paper V). Details regarding the test solutions and parameters are presented in the “Experimental” section, Tables 4 and 5.

The results (Paper V) showed that similar (for Fe and Mn) or even less (for Ni) amounts of metals were released into the complex forming solution of CA + KNO_3 compared with non-complexing test solution of KNO_3 at pH 3.1. This suggests protonation and corrosion/dissolution at defects/inclusions as the predominant metal release mechanisms.

In contrast, at pH values of 4.8 and 6.4, significantly higher amounts of released metals were observed from all investigated alloying elements in CA + KNO_3 compared to KNO_3 . This proposes a dominant complexation-induced metal release mechanism at weakly acidic or neutral pH values. This behaviour can be explained by the increase in the ionization of citric acid at weakly neutral pH range of 4.8, hence more complex formation with metal ions, as well as a lower extent of precipitation of released metals compared with conditions in the KNO_3 solution at these pH values.

Among the investigated alloying elements, Cr release showed the strongest dependency of citric acid at all investigated pH values. This is probably related to a higher solubility of Cr species in CA + KNO_3 compared with KNO_3 , verified by speciation/precipitation modelling of the investigated alloying elements.

Table 9: Changes in the predomination of the metal release mechanisms versus pH and the investigated alloying elements calculated based on the difference in the amount of released metals from grade 304 into KNO_3 and $\text{CA} + \text{KNO}_3$ test solutions (Paper V)

Element	pH	Which mechanism is predominant?
Fe	3.1	
	4.8	
	6.4	
Cr	3.1	
	4.8	
	6.4	
Mn	3.1	
	4.8	
	6.4	
Ni	3.1	
	4.8	
	6.4	

5.7.1 Complexation-induced metal release in citric acid: importance of surface and/or solution complexation

To assess whether complexation-induced metal release in citric acid containing solutions requires surface complexation, or solution complexation or both, 16.07 gL⁻¹ (35 wt% in water) polyacrylic acid (PAA) of 100 kDa (with pH values of 3.1, 4.8, and 6.4) was used as a complexation model compound, with the same number of carboxylic groups as 5 gL⁻¹ citric acid. PAA was separated from the abraded 304 stainless steel surface by means of a regenerated organic cellulose membrane of 3.5 kDa cut off to ensure that PAA could not reach the surface (experimental set ups, cells and parameters are presented in the “Experimental” Section, Tables 4 and 5). Between the stainless steel surface and the membrane, KNO₃ solution with the pH of interest (3.1, 4.8, or 6.4) was used as a non-complexing solution with some ionic conductivity to avoid the retention of metal ions within the membrane (Paper V).

This study clearly indicated that, at given test conditions (pH 3.1, 4.8, and 6.4; 40 °C; 5 gL⁻¹ citric acid) metal complexation (as the main metal release mechanism at weakly acidic / neutral pH) is of great importance. However, it could not be ruled out whether it is surface adsorption of protons (protonation, [125]) or dissolution at inclusions / defects, that are important at pH 3.1 (Paper V). The results strongly indicate surface complexation predominantly governs the metal release process, however, it can not be ruled out whether direct surface interaction is required or not. Literature findings on Fe and Cr dissolution by complex agents suggest ligand adsorption (as a first necessary step) followed by the metal-ligand detachment from the surface (which is the rate limiting step) [48, 60, 125, 126]. However, it should be noted that the adsorption of complex agents are pH- and temperature dependent [68, 84], and findings of this study may not be valid at lower and/or higher temperatures or pH values.

For instance, pH can have a significant effect on the adsorption kinetics of citrate on stainless steel surfaces (Paper V, [31]). While adsorption of citric acid at pH 4.8 on the abraded 304 surface completed after 1 h (except for Cr) was correlated with an initially strong increase in the amount of released metals followed by constant levels up to 24 h (Paper V), an earlier study on the same grade (results shown in Figure 5, Section 2.4) indicated that citrate starts to adsorb after 1 h at pH 2.4, which results in more metal release [31]. Therefore, further investigations are necessary in order to generalize the proposed metal release mechanisms of this study at higher temperatures, different pH values and for different alloying elements, which may be very important for risk assessment of food contact metals and alloys.

The proposed metal release mechanisms for grade 304 stainless steel in 5 gL⁻¹ citric acid (pH 3.1, 4.8, and 6.4, at 40 °C) are summarized in Figure 12. By considering the presence of surface defects and inclusions, which can contribute to the initial metal release of alloying elements, specifically Mn release (from inclusions) and Ni release (from surface defects), the following mechanisms are proposed for grade 304 stainless steel in 5 gL⁻¹ citric acid at given test conditions (pH 3.1, pH 4.8 and 6.4, at 40 °C):

- i) At pH 3.1, protonation (surface oxide dissolution by means of adsorbed protons) can be suggested as the main metal release mechanism after the initial exposure period. Initially, other mechanisms such as dissolution / corrosion due to the presence of defects / inclusions may be important (Paper V).
- ii) At pH of 4.8 and 6.4, surface complexation is suggested as the main metal release mechanism, which is time dependent (Paper V, [31]). It cannot be excluded that solution complexation may also play a role by hindering metal precipitation. However, it can be considered of minor importance for the release of Fe and Cr at these pH ranges since the passive surface oxide is

thermodynamically very stable and cannot be dissolved without having direct interaction with adsorbed citrates (Paper V).

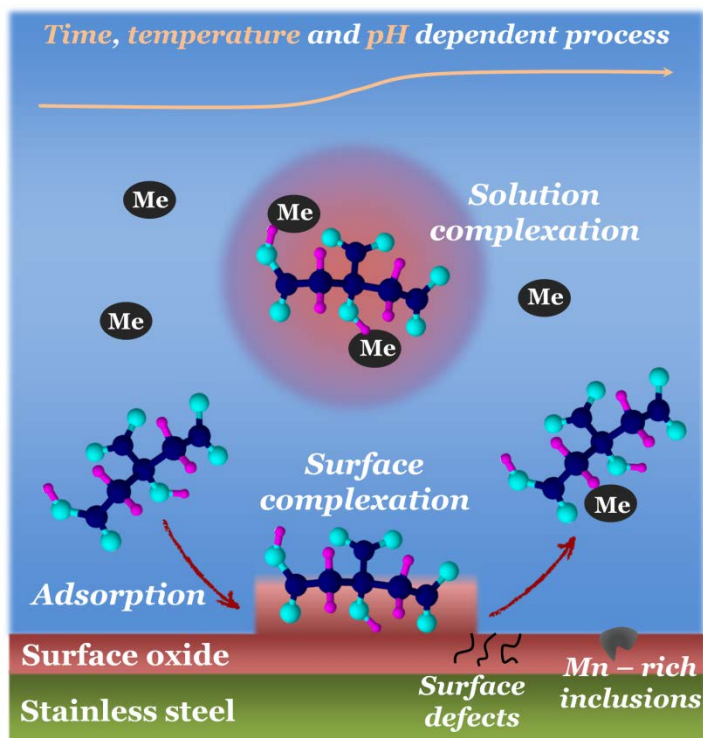


Figure 12: Schematic illustration of suggested metal release mechanisms for stainless steel grade 304 into citric acid solutions of weakly acidic / neutral pH and 40 °C, for abraded, 24h-aged and non-passivated surfaces.

6 Conclusions

The main objective of this doctoral thesis has been to provide an in-depth understanding of metal release processes, corrosion, and surface changes of different stainless steel grades in the presence of metal complex-forming agents, in particular citric acid. The results obtained within the framework of this thesis are expected to be used as a knowledge base for risk assessment of using different grades of stainless steels in food contact, or after passivation or cleaning of stainless steel with citric acid.

Based on the results and discussions of this thesis, the following main conclusions are drawn:

- Very low amounts of metals, with the preferential release of Fe and Mn, were released into citric acid (pH 2.4) during 10 days of exposure. These levels quantitatively correspond to an alloy mass loss of less than 0.000025 %. Low levels of metal release are attributed to the passive surface oxide. This oxide becomes enriched in chromium with time upon exposure in citric acid.
- None of the investigated alloying constituents of different tested grades of stainless steel were released in amounts exceeding their corresponding SRL values, stipulated in the CoE protocol
- An increased surface area to solution volume ratio (loading) can significantly enhance the concentration of metals in solution. Therefore, the outcome of the compliance test strongly depends on the application-specific surface area to solution volume ratio and must be taken into account.
- Cr was released as Cr^{3+} and no hexavalent Cr was released or detected either in complexing or non-complexing test solutions (pH 2.4-7.5).
- Fe (in citric acid and PBS solutions) and Mn (in all solutions) were preferentially released from all investigated

stainless steel grades. Ni was released to the lowest extent, as compared to its bulk alloy content.

- The amount of released metals largely depends on the surface conditions prior to exposure.
- Metal release from different grades of stainless steels into citric acid-containing solutions of varying pH generally followed the typical metal release behaviour of passive surfaces in the presence of complex agents; *i)* metal release is not proportional to the bulk composition, *ii)* initially higher release of all alloying elements followed by a significant reduction by time, *iii)* significant chromium enrichment in the outermost surface oxide.
- At acidic / weakly acidic pH, protonation can be proposed as the main important metal release mechanism for stainless steels. Other mechanisms such as dissolution / corrosion due to the presence of defects / inclusions may also induce metal release.
- At weakly acidic / neutral pH, surface complexation is proposed as the main metal release mechanism. Solution complexation may also play a role by hindering metal precipitation. However, it can be considered of minor importance for the release of Fe and Cr at these pH values due to the presence of a very stable passive layer that cannot be dissolved without direct surface interaction with adsorbed citrates.
- The released amount of all investigated alloying elements in metal complexing test solutions of pH 6.4 and pH 11 was significantly reduced compared to lower pH values of 2.4, 3.1 and 4.8. This is most probably due to a more stable surface oxide and precipitation of released metals.

7 Future work

In this thesis, metal release, surface changes and corrosion behaviour of different grades of stainless steels, relevant for food applications, have been investigated and several important factors and mechanisms were proposed. Future aspects that need to be taken into account are summarized below:

- Previous studies for non-passivated 304 coupons indicated that the presence of high chloride concentration (0.5 M NaCl) combined with citric acid at acidic pH (pH 2.2) or at weakly acidic pH (pH 4.8) (unpublished data), can induce a slightly higher amount of metal release compared with citric acid (pH 2.4) containing no NaCl (Paper III). SEM investigations of abraded 304 grades exposed into 5 gL⁻¹ citric acid (pH 4.8), 0.5 M NaCl (pH 4.8) and their mixed solution showed evident surface changes after exposure into the mixed test solution containing both citric acid and NaCl, while no visible changes could be observed upon exposures in solutions containing only citric acid or NaCl (unpublished data). More in-depth investigations are needed (e.g. XPS and AES analysis) to provide a better understanding of surface changes. This can be important for solutions containing both citric acid and chloride ions at high concentrations, such as edible seaweeds, which are increasingly consumed as part of the modern Western diet. Chloride concentrations as high as 3.5-134 g kg⁻¹ have been reported for different commercially available seaweeds in New Zealand [127].
- Investigations of the complexation ability of other complex forming agents, e.g. food related proteins such as casein, alone or in combination with other metal complex agents such as citric acid are highly recommended for a better understanding of possible metal release mechanisms of

large importance for the risk assessment of alloys in food contact.

- This study did not consider the effect of impurities / inclusions and defects on the metal release mechanism. Therefore, other investigations, (e.g. AFM) are suggested to distinguish their possible influence on corrosion / dissolution and metal release behaviour of stainless steels.
- Further studies should further clarify the metal release mechanisms, and quantify their individual importance for stainless steel in citric acid solutions of varying temperature and pH.

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