



Inappropriate cleaning treatments of stainless steel AISI 316L caused a corrosion failure of a liquid transporter truck



Valentin Romanovski^{a,b,c,*}, Vitali Frantskevich^d, Vitali Kazlouski^d, Aliaksandr Kasach^d, Andrei Paspelau^d, Yolanda Hedberg^a, Elena Romanovskaia^d

^a Department of Chemistry, Division of Surface and Corrosion Science, KTH Royal Institute of Technology, SE-100 44, Drottning Kristinas väg 51, Stockholm, Sweden

^b Institute of General and Inorganic Chemistry, National Academy of Sciences of Belarus, 220072, Surganova st., 9/1, Minsk, Belarus

^c Science and Research Centre of Functional Nano-Ceramics, National University of Science and Technology "MISIS", 119049, Lenin av., 4, Moscow, Russia

^d Belarusian State Technological University, 220006, Sverdlova st., 13, Minsk, Belarus

ARTICLE INFO

Keywords:

316L steel
Corrosion
Pitting
Chlorine
Car shampoo
Latex remover

ABSTRACT

Corrosion of transport tanks for transporting aggressive liquids is undesirable from both economic, safety, and sustainability perspectives. It is thereby not only important to consider the composition of the aggressive liquids to be transported and the material of the tank, but also the composition of the cleaning liquids and procedures. Triggered by an industrial case, we investigated the extent of corrosion during cleaning treatments and simulated contact with transported fluids at relevant conditions. Corrosion of stainless steel AISI 316L was investigated in commercial latex remover liquid, 90 wt% acetic acid, two different car shampoos, and solution of potassium hydroxide at room temperature. After electrochemical, solution analytical, and surface analytical analysis of the transporter tank material and some of the transported and cleaning fluids, we found that even a short time of use of non-licensed latex remover liquid could trigger a self-sustaining mechanism for pitting corrosion of stainless steel AISI 316L.

1. Introduction

Transportation of liquids in certain automobile tanks represents an important fraction of the total number of cargos transported by road. Different types of substances have their own safety handling rules during transportation and storage. Corrosive substances, such as acids and bases, are strictly regulated, as well as explosive and burnable substances such as organic solvents. Each substance has special requirements for the container material and the equipment. Hence, the cost of automobile tanks is very high and their failure is a serious problem both from an economic, a safety, and a sustainability perspective.

The reasons for corrosion can be very diverse, including a combination of factors such as the substances transported, the quality of the metal from which the tank is made, and the cleaning agents used for internal surfaces. In case of corrosion-induced failure, it is therefore necessary to understand its specific nature in order to take effective steps for its prevention and mitigation.

Transport materials for corrosive media are often made of stainless steel AISI 316L, which contains chromium, nickel, and molybdenum as alloying components and a low carbon content. The low carbon content reduces the likelihood of corrosion of

* Corresponding author at: 220072, Surganova st., 9/1, Minsk, Belarus.

E-mail addresses: vramano@kth.se (V. Romanovski), fvs2@tut.by (V. Frantskevich), kasach2018@bk.ru (A. Kasach), yolanda@kth.se, yhedberg@uwo.ca (Y. Hedberg), elenaro@kth.se (E. Romanovskaia).

<https://doi.org/10.1016/j.engfailanal.2020.104938>

Received 8 May 2020; Received in revised form 19 August 2020; Accepted 17 September 2020

Available online 22 September 2020

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austenitic steels when exposed to a welding thermal cycle [1]. Molybdenum contributes to the binding of carbon and nitrogen in the form of compounds that are insoluble in the austenitic matrix, which increases the resistance to stress corrosion cracking [2,3]. Low carbon and high molybdenum further increase the resistance to pitting and crevice corrosion in the presence of chlorides and halides [4,5]. At least 13–15 wt% chromium significantly increases the corrosion resistance of the stainless steel by forming a passive chromium-rich oxide.

The passive oxide layer on stainless steel is spontaneously formed in air and water, and is very thin, usually in the range of 10–100 Å. This layer contains both chromium oxide and iron oxide [6]. The passive surface oxide on austenitic stainless steels consists of an inner layer and an outer layer [7]. The formed oxide layer and its chemical structure depends on the environment, such as the pH of the solution and the presence of complexing agents [8–10].

The material of transport containers for corrosive media is usually selected based on compatibility with the transported media and to minimize corrosion. However, when cleaning the internal surface of the container, various detergents, both alkaline and acidic, are used. Most cleaning agents are alkaline (containing sodium or potassium hydroxide and some additives, such as surfactants and chlorine-containing disinfectants). Those agents clean surfaces well from fats and other organic compounds, including acids. In some cases, however, companies prefer to use cleaning agents that clean stainless steel surfaces as quickly as possible. Such solutions could be complex acidic solutions.

When studying the effect of acetic acid on the corrosion of 316L, it was found that the passive-active transition threshold strongly depended on the concentration of acetic acid [11]. While 70% acetic acid resulted in an activation of the passive 316L, no such effect was observed in 90% acetic acid. It is well-known that chloride ions influence the corrosion of stainless steel. This occurs often by localized corrosion types, which depend on factors such as chloride concentration, pH, agitation, geometry, stainless steel grade, microstructure, and surface preparation [12–14]. Synergistic effects of acetic acid and sodium chloride on pitting corrosion have also been reported [15]. Synergistic effects of chlorides and citric acid at neutral pH were furthermore found previously for non-passivated surfaces of stainless steel grade AISI 304 [16].

Depending on the pH and concentration of sodium hydroxide, alkaline solutions used as cleaning agents could theoretically affect stainless steel corrosion. Effects of sodium hydroxide on the passivation capacity of 316L and similar stainless steel grades are however small at low temperatures [17,18]. Sodium hydroxide was reported to be detrimental to the corrosion resistance of 316L at higher temperatures than 35 °C and at concentrations of 40 and 50% of sodium hydroxide [8,19].

The aim of this study was to investigate a corrosion case of a transporter in 316L exposed to several corrosive fluids and non-licensed cleaning agents, and to provide comparative data on 316L corrosion susceptibility in commercial latex remover liquid, 90 wt % acetic acid, two different car shampoos, a solution of potassium hydroxide, and diluted nitric acid at room temperature.

2. Methodology

2.1. Analysis of bulk composition, surface, and corrosion products

A x-ray fluorescence spectrometer Axios (PANalytical, the Netherlands) was used for an elemental analysis of the stainless steel (from untreated and non-affected locations), analyzing elements with atomic numbers ranging from O (oxygen) to U (uranium) at concentrations from 10^{-5} to 100 wt%.

The surface morphology and elemental composition of the corrosion products was investigated by means of a JEOLJSM-5610LV scanning electron microscope (SEM) equipped with a chemical micro-X-ray spectroscopic analysis system (EDS) with an accuracy of 0.1 wt%. The magnification was up to 2000 times.

2.2. Sample preparation

For analysis of corrosion products and pits of the corroded areas, samples were cut from affected areas of the stainless steel container, which was of grade AISI 316L according to the owners and the certificate of the container.

Otherwise, stainless steel samples were cut from unaffected locations of the stainless steel container, with a thickness of 4 mm and dimensions of 20 × 20 mm. They were then abraded with emery papers down to FEPA P 1200# SiC grit and polished using short synthetic DP-Nap and diamond pastes (down to 1 µm, DP-Stick P Struers). The samples were thereafter rinsed with distilled water, degreased by acetone and ethanol (for 5 min each), and dried by nitrogen gas at room temperature (≈ 21 °C). All stainless steel samples were kept in a desiccator at room temperature for 24 ± 2 h prior to testing.

2.3. Solutions and chemicals

According to information from the owner, the cleaning procedures must have been involved in the corrosion failure, as the transported liquids have not caused corrosion failures without that cleaning. According to information from the owner on all cleaning and transported liquids, the following solutions were selected:

- solution 1 (cleaning agent) – acidic detergent for latex removal M3140 (commercial product)
- solution 2 (cleaning agent) – diluted 1:5 car shampoo Active Foam (anionic surfactant 5–15%, nonionic surfactant $\geq 5\%$, sodium hydroxide $\leq 5\%$, complexing agents $\leq 10\%$, organic solvents $\leq 5\%$ – commercial product)
- solution 3 (frequently transported liquid) – 90 wt% acetic acid of reagent grade of purity

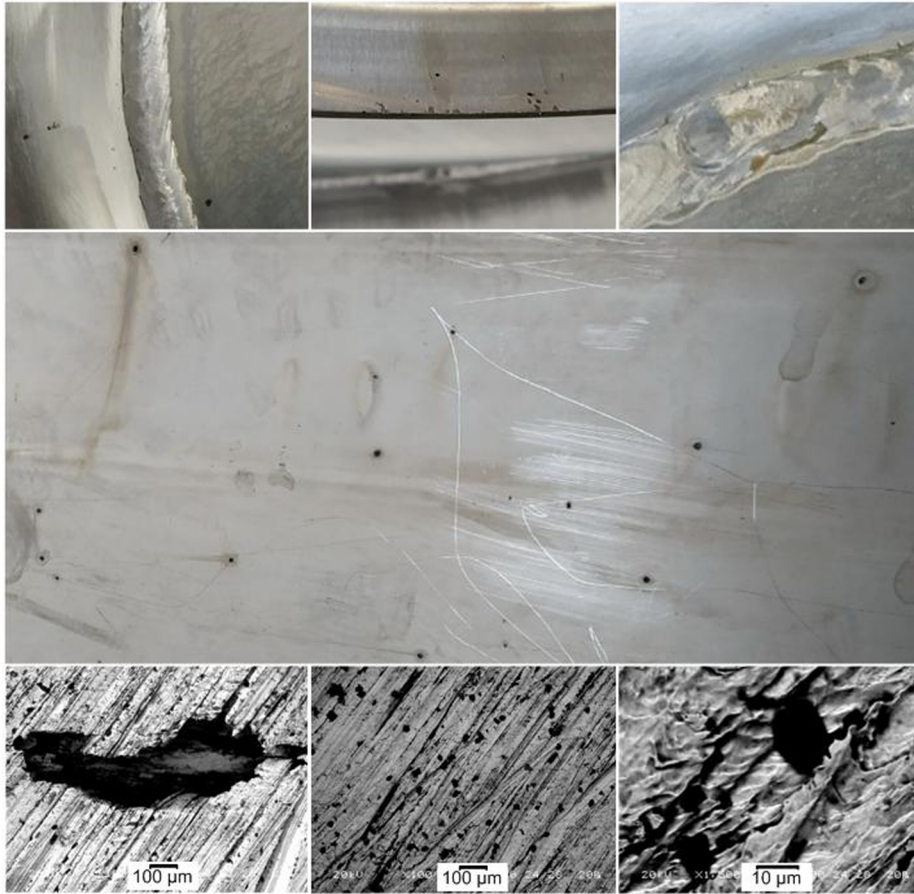


Fig. 1. Photographs (upper two rows) and SEM images (lowest row) showing millimeter- and micrometer- sized pits and visible corrosion at cutting and welding seams (upper row) of the stainless steel container surface.

- solution 4 (cleaning agent) – solution of potassium hydroxide of reagent grade of purity
- solution 5 (cleaning agent) – 10 wt% of car shampoo BK-1 (commercial product)

The selected solutions represented all used cleaning agents and the worst-case transported liquid.

The transported liquids were usually stored in a tank up to 2 days. During the cleaning procedure, the contact of cleaning solutions was up to 60 min. The volume of transported liquids in the tank has been 30 m³.

2.4. Electrochemical studies

A Metrohm Autolab PGSTAT 302 N potentiostat/galvanostat with three-electrode cells (100 mL), an Ag/AgCl reference electrode in saturated KCl, a Pt grid counter-electrode, and the stainless steel sample (0.785 cm²) as a working electrode, prepared as described in the section “sample preparation”, were used for the electrochemical measurements. All measurements were performed at room temperature (≈ 21 °C) and repeated at least three times. The solutions were not deaerated. Potentiodynamic polarization was obtained with a scan rate of 1 mV/s in the range from -200 to $+ 200$ mV relative to the open circuit potential, which was first determined for 5 min.

3. Results and discussion

Fig. 1 shows photographs and SEM images of a corroded stainless steel container used for the transportation of corrosive fluids. The photographs (upper two rows in **Fig. 1**) show pits up to 8 mm in diameter.

The majority of corrosion defects were attributed to pitting corrosion, **Fig. 1**. These occur preferentially along weak points such as weld and cutting seams, **Fig. 1**. The SEM images (**Fig. 1**) show extensive pits sized 5–30 µm. Obviously, this container material has failed and there was a substantial risk of leakage or accidents associated to this corrosion failure.

Fig. 2 shows an example of a shallow pit. Cracks were visible around most pits and at the bottom of pits. Cracks along the end of the sample cut out for the investigation were even several centimeters long, indicating a susceptibility to cracking. Corrosion products

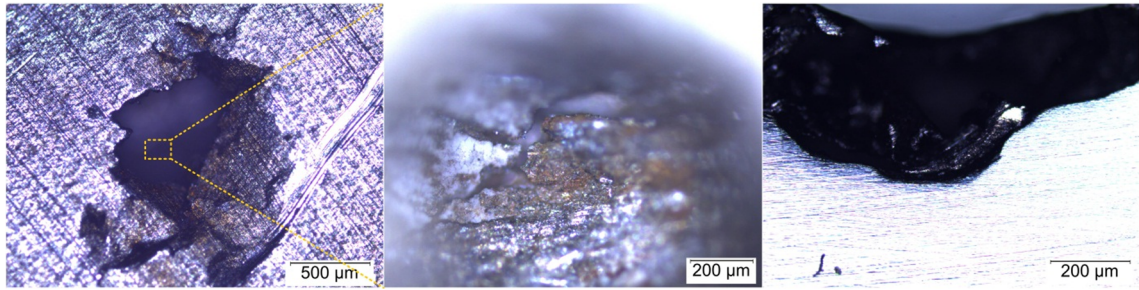


Fig.2. Morphology of shallow pits as imaged by optical microscopy. Left: overview image; middle: magnification of the corrosion products visible in the shallow pit of the left image; right: edge of shallow pit, showing the passive (cathodic site) stainless steel surface and the active (anodic site) shallow pit.

were clearly visible in these shallow pits, but not on the unaffected surface, highlighting the localized nature of this corrosion attack.

The nominal bulk composition of the stainless steel container and the composition of some transported liquids and cleaning agents were analyzed. The composition of the stainless steel measured by XRF complies with the composition of AISI 316L stainless steel, [Table 1](#). The main alloying elements (nickel, chromium, and molybdenum) were at the lower range of allowed ranges.

According to information from the owner of the container, the transported media in the container consisted of acids, organic solvents of various nature (alcohols, polar and non-polar aromatic compounds, organic nitrates, solvents), oils, and fats of various origin. For cleaning, 50% potassium hydroxide and other alkaline solutions were mainly used. According to [\[20\]](#), the presented list of substances was mostly classified as corrosion class A, while some substances were classified as corrosion class B, such as, for example, 90% acetic acid. Therefore, 90 wt% acetic acid was included in the investigation.

Corrosion should not be caused by using alkali, for example potassium hydroxide, for cleaning of transportation materials, or by concentrated acetic acid and acetic acid at concentrations up to 50% according to [\[20\]](#). Solutions of sodium hydroxide and acetic acid at 80% could result in minor corrosion and cause a change in surface color according to [\[20\]](#). The remaining transported liquids should not cause corrosion of this stainless steel grade. Hence, all cleaning agents and 90 wt% acetic acid were selected for the investigation.

Acetic acid (solution 3) and the latex remover solution (solution 1) have an acidic pH of 1.6–1.7. The latex remover has been periodically used to wash the internal surface of the stainless steel container. This solution is not recommended for cleaning stainless steel according to the internal cleaning rules. It is used from own stocks of the organization that owned the transporter container.

In order to investigate which substances caused the extensive corrosion of the stainless steel container, the corrosion products were analyzed. SEM images are presented in [Fig. 3](#) and corresponding EDS results are shown in [Table 2](#).

Based on the investigation of the corrosion products, chlorine-, sulfur-, and nitrogen-containing species, or a combination of those, contained in liquids (transported or cleaning liquids) were considered to be the main candidates for the corrosion failure. Therefore, some selected media submitted by the container owner were selected for electrochemical studies. In addition, a 0.1 M solution of nitric acid was also investigated, as its formation is possible following partial decomposition of the transported nitrate-organic

Table 1

Measured composition of the investigated stainless steel sample and the standard composition for 316L (EN1.4404) stainless steel.

Element	Sample	EN1.4404
O	1.21	–
C	N/A	< 0.03
N	N/A	< 0.11
S	N/A	< 0.015
Na	0.10	–
Mg	0.07	–
Al	0.10	–
Si	0.80	< 1.0
P	0.03	< 0.045
Cl	0.05	–
V	0.09	–
Cr	16.46	16.5–18.5
Mn	1.19	< 2.0
Fe	67.18	in balance
Co	0.45	–
Ni	9.84	10.0–13.0
Cu	0.296	–
Mo	2.146	2.0–2.5

N/A – not analyzed

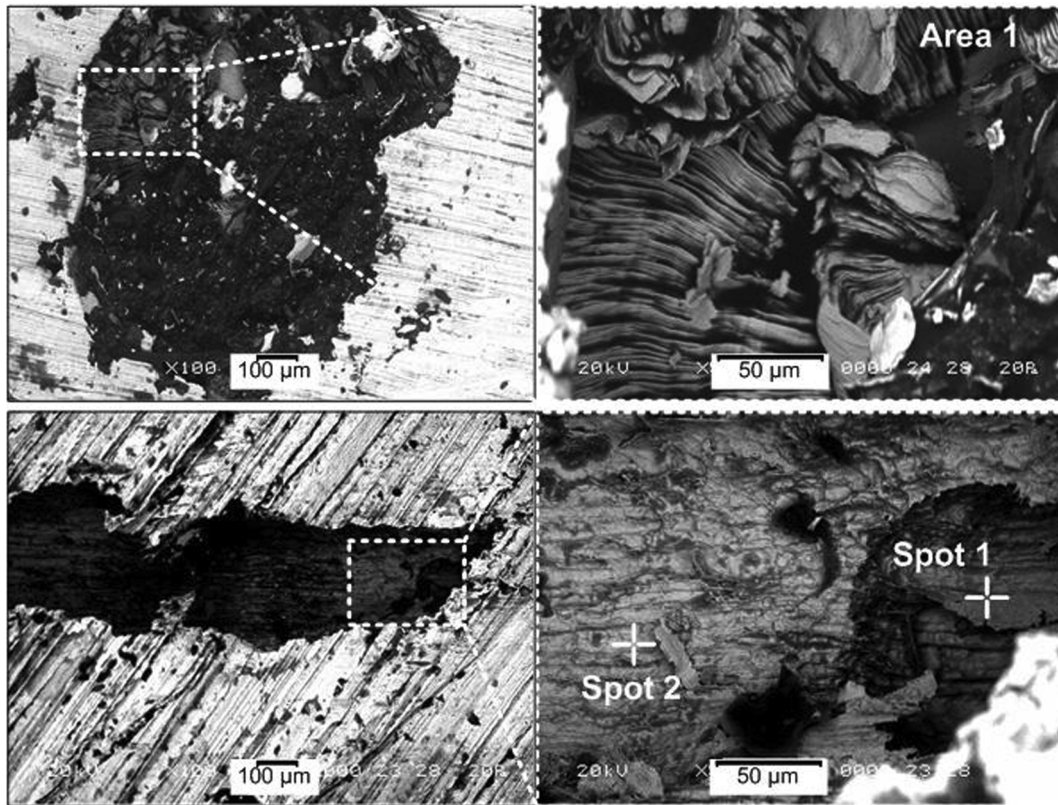


Fig. 3. SEM images of analyzed corrosion products with corresponding EDS results in Table 2.

Table 2

Composition by means of EDS analysis (average) of corrosion products shown in Fig. 3. Significantly deviating numbers are marked in bold for guidance.

Element	Area 1		Spot 1		Spot 2	
	wt.%	at.%	wt.%	at.%	wt.%	at.%
N	–	–	5.2	17.2	8.0	24.9
Mg	9.0	17.3	0.7	1.3	0.3	0.5
Al	2.9	5.1	1.1	1.9	1.6	2.6
Si	2.5	4.1	1.6	2.7	1.1	1.8
S	1.8	2.6	–	–	–	–
Cl	0.0	0.0	0.3	0.3	–	–
Ca	0.6	0.7	0.1	0.2	0.2	0.3
Cr	13.6	12.3	16.7	15.0	16.9	14.2
Mn	0.6	0.5	1.7	1.5	1.4	1.1
Fe	61.4	51.3	63.4	53.0	60.6	47.5
Ni	7.6	6.1	8.00	6.4	8.7	6.5
Mo	–	–	1.3	0.6	1.3	0.6

compounds. Representative curves of potentiodynamic polarization, along with solution pH and corrosion current density values (i_{corr} , $\mu\text{A}/\text{cm}^2$) are presented in Fig. 4. Corresponding corrosion parameters are presented in a Table 3.

The greatest corrosion current densities were observed for solutions 1 and 3 (acidic detergent and acetic acid), respectively. For solutions 5 and 6 (car shampoo BK-1 and 0.1 M nitric acid), the lowest corrosion current densities were observed (one order of magnitude lower). In solution 3 (90% acetic acid), a very high corrosion potential (0.85 V vs. Ag/AgCl sat. KCl) was found. Comparison with literature data reveals that this high corrosion potential is probably related to a too high solution resistance [11], although the obtained corrosion current density of $0.5 \mu\text{A}/\text{cm}^2$ seems reasonable compared with findings at higher temperature (90 °C) in the mA/cm^2 range [11]. In solution 1 (the acidic detergent), there was an indication of pitting corrosion anodic to the potential of about 0.45 V vs. Ag/AgCl sat. KCl. Also, its corrosion potential was more positive as compared to solution 6 (0.1 M nitric acid) with a similar pH and literature data in diluted hydrochloric acid at pH 1.7 [21], indicative of oxidizing species. The lowest corrosion current density in 0.1 M nitric acid was also associated with the lowest passive current density at $1.9 \mu\text{A}/\text{cm}^2$.

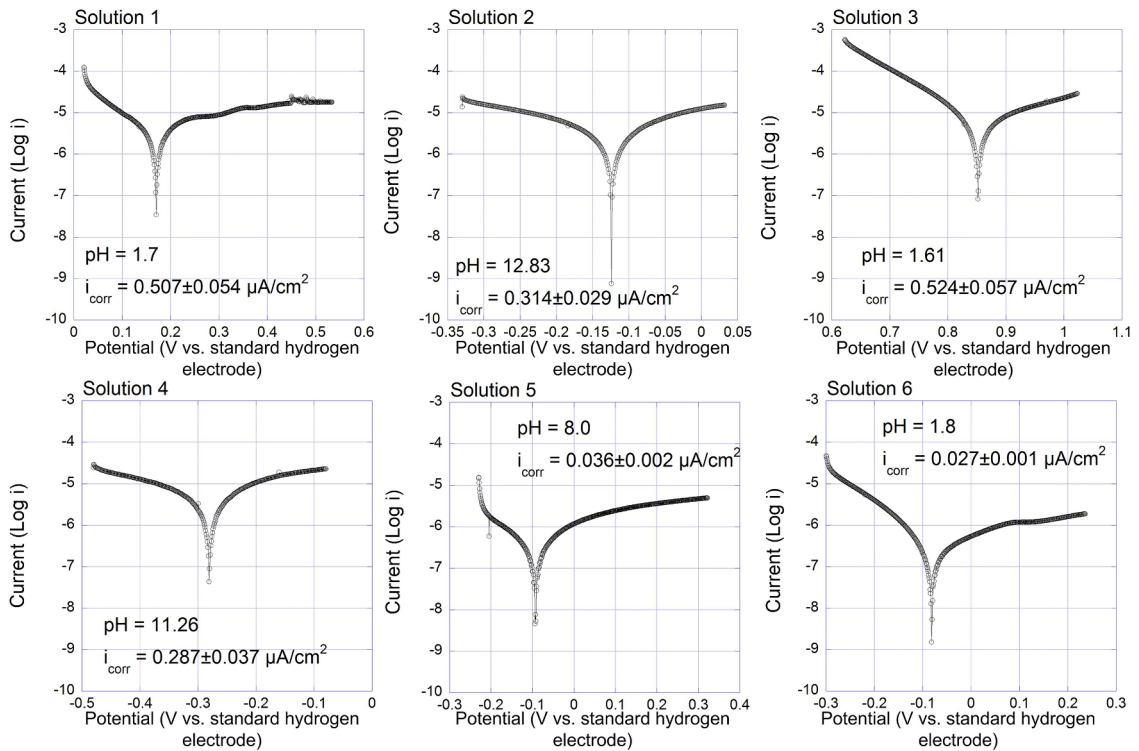


Fig. 4. Representative curves of potentiodynamic polarization at room temperature for six selected solutions: 1 – acidic detergent, 2 – car shampoo Active Foam, 3 – 90 wt% acetic acid, 4 – solution of potassium hydroxide, 5 – car shampoo BK-1, and 6 – 0.1 M nitric acid. The inset corrosion current density values (i_{corr} , $\mu\text{A}/\text{cm}^2$) show mean and standard deviations of at least three measurements.

Table 3

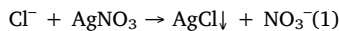
Corrosion potential (E_{corr}), corrosion current density (i_{corr}), and passive current density (i_{pass}), as determined from + 200 mV vs. E_{corr} , respectively. Mean and standard deviations of at least three replicate measurements are shown. Solutions: 1 – acidic detergent, 2 – car shampoo Active Foam, 3 – 90 wt% acetic acid, 4 – solution of potassium hydroxide, 5 – car shampoo BK-1, and 6 – 0.1 M nitric acid.

Solution	E_{corr} , V	i_{corr} , $\mu\text{A}/\text{cm}^2$	i_{pass} , $\mu\text{A}/\text{cm}^2$
1 (pH 1.7)	0.17 ± 0.027	0.507 ± 0.031	17.78 ± 4.5
2 (pH 12.8)	-0.12 ± 0.022	0.314 ± 0.036	15.13 ± 2.6
3 (pH 1.6)	0.85 ± 0.041	0.524 ± 0.059	28.84 ± 3.1
4 (pH 11.3)	-0.28 ± 0.018	0.287 ± 0.043	22.04 ± 6.1
5 (pH 8.0)	-0.092 ± 0.014	0.036 ± 0.026	4.95 ± 1.8
6 (pH 1.8)	-0.081 ± 0.025	0.027 ± 0.009	1.88 ± 0.7

In order to further investigate the pitting and corrosion susceptibility of 316L in the different solutions at open-circuit conditions, specimens were also immersed in the selected solutions for 6 days (144 h). SEM images after this immersion are presented in Fig. 5.

The immersion tests also identify the acidic detergent as the most corrosive. The stainless steel specimen visually dissolved in that medium. Also, the acetic acid caused localized corrosion with many pits, Fig. 5d. Table 4 presents the composition (measured by EDS) of the initial and treated (after immersion to acidic detergent) surfaces.

Based on the EDS results of scratched-off corrosion products (table 2 and table 3), it is concluded that the used acidic detergent contains compounds with sulfur and chlorine. To confirm the presence of chlorides in the acidic detergent, a qualitative reaction to the chloride ion was carried out using silver nitrate by the reaction



The addition of silver nitrate to the solution of acidic detergent produced characteristic white flakes of silver chloride, which after deposition formed a characteristic white precipitate.

Thus, the acidic detergent was found to have the greatest corrosive effect on 316L steel. The use of solutions containing high amounts of chlorides at acidic conditions is unacceptable for stainless steel 316L [22–24]. In addition, judged from its relatively higher corrosion potential, this acidic detergent solution contained most probably oxidizing species, maybe hypochlorites or hydrogen peroxide, that in a synergistic effect increase the susceptibility to pitting corrosion of stainless steel grade 316L that otherwise would resist chlorides [25].

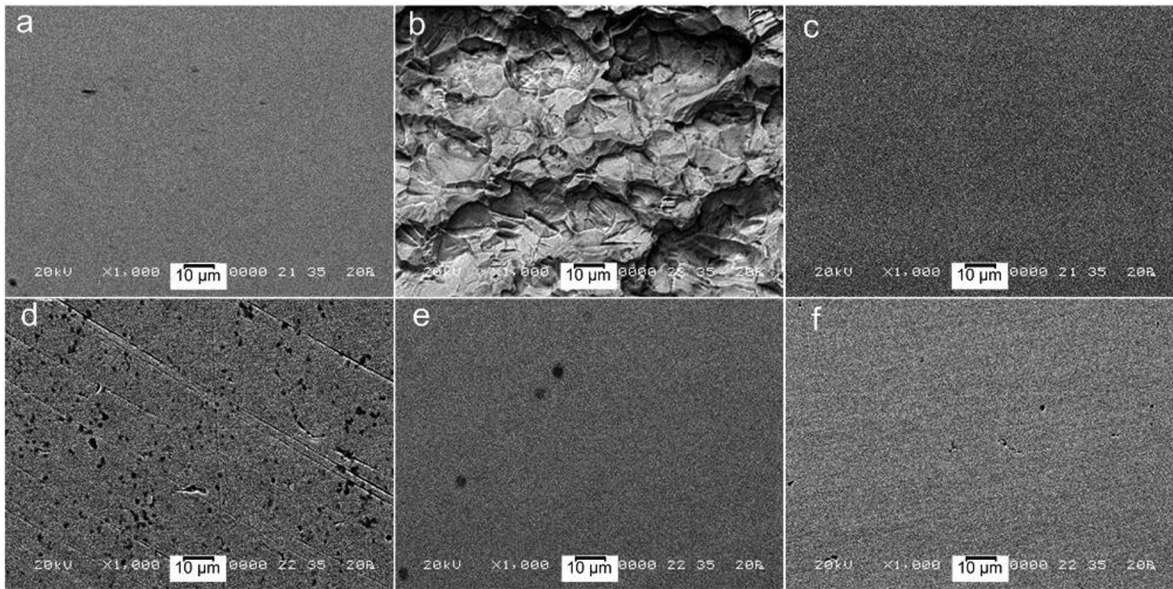


Fig. 5. SEM images of the investigated 316L specimens after immersion for 144 h at room temperature in a) without treatment, b) acidic detergent (solution 1), c) car shampoo Active Foam (solution 2), d) 90 wt% acetic acid (solution 3), e) solution of potassium hydroxide (solution 4), and f) car shampoo BK-1 (solution 5).

Table 4

Composition (wt.%) of initial 316L surface and after immersion (144 h) to acidic detergent solution, as measured by EDS.

Element	Initial surface (Fig. 5 a)	After immersion in acidic detergent	
		Surface (Fig. 5 b)	Scatched-off corrosion products
Si	0.75 ± 0.07	0.55 ± 0.07	2.95 ± 1.48
S	0.00 ± 0.00	0.05 ± 0.07	2.40 ± 1.70
Cl	0.00 ± 0.00	0.15 ± 0.07	4.75 ± 0.78
K	0.05 ± 0.07	0.10 ± 0.00	6.75 ± 1.20
Ca	0.05 ± 0.07	0.00 ± 0.00	2.00 ± 0.57
Cr	17.8 ± 0.64	18.8 ± 0.49	15.9 ± 0.92
Fe	68.8 ± 0.42	69.3 ± 1.13	52.5 ± 0.28
Ni	9.80 ± 0.57	8.85 ± 0.35	8.30 ± 0.14
Mo	2.80 ± 0.28	2.25 ± 0.21	4.50 ± 2.26

The 316L stainless steel container material in this study has been used for transportation of different corrosive liquids and has been cleaned with a non-licensed, chloride containing, oxidizing, and acidic cleaning agent originally intended for the removal of latex from surfaces. Our investigation points out that the cleaning agent, possibly in combination with the transport of acetic acid, was most probably the main factor for corrosion failure and should be avoided in future use. During cleaning, the stainless steel surface was activated and formed pits. These pits, still containing some chlorine-containing species, were then most probably the anodic sites, while the remaining surface was the cathodic site, driving localized corrosion and hindering the chlorides to detach. Negatively charged chlorides are instead attracted and enriched at the pit bottom due to electrostatic interactions (more positive charges of protons and metal cations) [26]. The chlorine-containing species may therefore not leach out by other media and could continue to react in the subsequent exposure to acetic acid. A synergistic effect of acetic acid and chlorides on pitting corrosion of stainless steel has previously been suggested in [15].

The other transported or cleaning liquids of neutral or alkaline pH did not have any severe effect on corrosion in our comparative investigation.

The observed enrichment of chromium, nickel, and molybdenum in corrosion products is probably correlated with a selective dissolution of iron at acidic conditions and in the presence of chlorides [27,28]. Molybdenum is in addition known to precipitate at acidic conditions, while it is solubilized in neutral/alkaline conditions [29], which is an important function for increasing the pitting corrosion resistance of stainless steels [30].

In the case of transportation of various organic liquids, including solvents, the possibility of using barrier coatings in the form of paints and varnishes is excluded. The literature presents studies of suitable coatings for stainless steel 316L as silicon oxide [31], aluminum oxide [32], silane-vapriole [33], but this applies more to exploratory research and is hardly applicable for the case under consideration. The addition of corrosion inhibitors or organic compounds [34] is also unsuitable, as this would lead to pollution of the

transported media. Instead, the best way to increase the lifetime of 316L transporter containers for corrosive liquids is to use suitable cleaning agents.

This study highlights the importance of even single-use cleaning treatments. Our study is limited by the experimental boundary conditions (such as type of investigated media and temperature), comparing a number of candidate liquids at room temperature by a six-day immersion test and potentiodynamic polarization focusing on the corrosion current density. The presented potentiodynamic polarization curve and derived corrosion current density in 90% acetic acid is probably erroneous due to limited ionic conductivity in that medium [11], however, consistent with literature findings and immersion test results.

4. Conclusion

Most probably, the use of a cleaning agent intended for removing latex residues combined with the transportation of acetic acid was responsible for the severe corrosion failure of a 316L stainless steel container used for the transportation of corrosive liquids. The cleaning agent contained chlorine and sulfur species, had an oxidative effect, and acidic pH. The stainless steel visually dissolved in that medium during a 6 days immersion test. Also 90 wt% acetic acid was inducing severe pitting corrosion. The corrosion products of the investigated case contained species of chlorine, sulfur, and nitrogen. Most probably, the combined action of using a – for this application unintended – acidic, chloride-containing, and oxidative cleaning agent with the subsequent transport of 90% acetic acid accelerated the corrosion further in a synergistic way.

CRedit authorship contribution statement

Valentin Romanovski: Conceptualization, Methodology, Investigation, Visualization, Writing - original draft. **Vitali Frantskevich:** Investigation. **Vitali Kazlouski:** Investigation. **Aliaksandr Kasach:** Investigation, Data curation, Formal analysis. **Andrei Paspelau:** Investigation. **Yolanda Hedberg:** Data curation, Formal analysis, Writing - review & editing. **Elena Romanovskaia:** Data curation, Formal analysis.

Declaration of Competing Interest

Authors declare no competing interests.

Acknowledgements

The authors gratefully acknowledge the financial support of the Ministry of Science and Higher Education of the Russian Federation in the framework of Increase Competitiveness Program of NUST «MISI» (№ K2-2019-007), implemented by a governmental decree dated 16th of March 2013, N 211.

Data Availability

Some or all data, models, or code that support the findings of this study are available from the corresponding author upon reasonable request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.engfailanal.2020.104938>.

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