

Information

on Stainless Steel Surfaces
in Steam Sterilizers

Foreword

When processing medical products, a high level of quality is absolutely critical. The mission of the German Society of Sterile Supply (DGSV e.V.) is to improve the overall quality of medical products processing. One of the ways to achieve this quality improvement is by increasing process reliability, which is our primary objective. The patient is the focus of everything we do. In addition to this, actual industry experience can also help to improve quality. Rouging is a well known quality issue in the steam sterilization process. But what actually causes rouging, and how can operators eliminate these causes and prevent them from becoming a problem? In this brochure, you'll find a description of this very quality issue, as well as steps that you can take to successfully address both the issue itself and its causes.

Maik Roitsch
DGSV Chairman

Authors' Note

Dear Readers,

This brochure from the German Workgroup for Chambers (German abbreviation: AKK) deals with the topic of rouging, with a focus on chamber discolouration on stainless steel sterilizer walls. We have taken great care in preparing this brochure. Each the employees involved discussed and evaluated the vast array of different information and viewpoints in a series of meetings held by the Working Group. This document is the result of their hard work.

The wealth of technical information it contains is intended to assist you with inspecting the chamber interiors of your steam sterilizers and performing a risk analysis regarding the formation of deposits and chamber discolouration. On the other hand, this information is also provided as an illustration of just how multifaceted the assessment of factors that influence changes in the interior surfaces of stabilizer chambers can be. We've created this informational brochure to help you draw the proper conclusions whilst also avoiding premature, and potentially even incorrect, assessments and measures.

We hope you enjoy reading it!

The Authors

General Information

The utmost care was used in creating this brochure from the German Workgroup for Chambers (AKK). Despite this level of care, the document may still contain errors. The authors do not assume legal responsibility or any form of liability for erroneous information contained herein or the potential consequences thereof.

The authors welcome suggestions for improvement and are happy to be notified of any errors.

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Notes

Introduction

When medical instruments are reprocessed, they are sterilized in steam sterilizers that have been specially optimised for the task at hand. As a concept that has been known about for years, steam sterilization is a well researched and reliable processing method. For the technical design of the chambers, high-alloyed austenitic stainless steel alloys, such as 1.4301, 1.4404, 1.4571, and other similar alloys, are used as structural materials. Figures 1 and 2 show examples of a typical steam sterilizer, with a view of the sterilization chamber interior.

In many application cases, actual operating experience has shown that, over the course of the sterilization chamber's service life, undesired discolouration often appears on the initially bright finish of the stainless steel regions. These types of changes in supposedly rust-resistant stainless steel surfaces (see Figure 2) are often disconcerting to the employees in charge of the MPPU/CSSD (medical products processing unit / central sterile services department) and to those responsible for instrument processing.

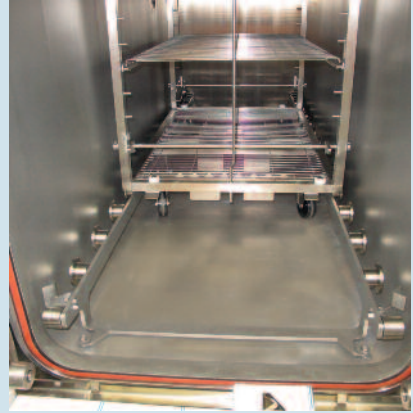


Figure 1: Typical image of a chamber in good order (source: Belimed)

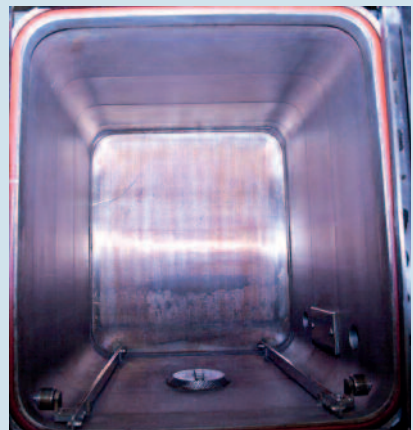


Figure 2: Condition of a chamber after repeated use (visible chamber discolouration) (source: Belimed)

The goal of this guide is to provide an in-depth explanation of the, in some cases, extremely complex interrelated causes behind the changes described above, and to also present various different influencing factors. However, we should start by noting that these type of surface alterations are typically the result of several different factors that can even interact with and/or exacerbate one another depending on the individual scenario.

The usual response when analysing the causes behind the discolouration problems (which vary greatly in terms of individual tenacity) found in connection with the typically unfamiliar deposits on stainless steel surfaces is to first contact one or more of the following groups: building services, the manufacturer of the WD and the suppliers of the process chemicals used.

Each of the aforementioned points of contact approaches the issue of discolouration / (undesired) film on the stainless steel surfaces selectively, from its own individual, subjective perspective, and may then reply that its system or product is working flawlessly, and is therefore not responsible for causing the discolourations. From an operator's point of view, this approach is usually not very helpful for the problem analysis that needs to be performed, nor is it conducive to effectively resolving the problem.

When analysing the root cause, it is important to first check the quality of the water being supplied to the devices, as well as the composition of the condensate from the sterilizing steam.

In addition, a chemical-physical analysis of swab/abrasion samples taken by a specialist from the discolourations on the affected stainless steel surfaces is recommended. The interpretation of the results from this analysis will allow initial conclusions to be drawn about the sources and causes of the film.

However, it is entirely possible that, even if all of the necessary media-supply parameters are complied with, permanent films/discolourations can appear on the interior surfaces of sterilizer chambers.

This brochure provides basic and supplementary tips and information about the potential causes of surface discolourations, as well as recommendations for dealing these typically bothersome phenomena.

The illustrations and figures accompanying the text help to ensure that the entire scope of the problem, including all of the related factors, is covered. Particular attention has been given to explaining the topic of steam sterilization and how potential causes of discolouration can occur in this context.

At this junction it should be noted that, as what is referred to as form of uniform corrosion, these films/discolourations on stainless steel surfaces can also be caused by a host of other extremely diverse influencing factors aside from the rouging effect described in this brochure. Discolourations and corrosion-related alterations in the surface of non-corrosive stainless steel alloys can, for example, have the following known causes:

- ➔ Inadequate quality of water or steam
- ➔ Chamber surfaces that were not manufactured properly and/or in conformity with standards
- ➔ Unsatisfactory alloy quality
- ➔ Application of unsuitable methods for working stainless steel surfaces
- ➔ Unsuitable manufacturing techniques used in producing the chamber
- ➔ Unsuitable substances in the sterilization materials
- ➔ Introduction or carry-over of chemicals into the chamber
- ➔ Chemical indicators or stickers
- ➔ Chemical attacks on the chamber or loading trolleys, e.g. through the use of chemicals not suitable for cleaning
- ➔ Secondary processes posing corrosion risks (e.g. fretting corrosion, pitting, contact corrosion, etc.)

In each specific case, other factors may also come into consideration as a potential cause.

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1. Water and its effects

The use of untreated water (= tap water) for the technical application described herein is not advisable, since this type of water does not possess the necessary level of purity in most cases. For this reason, tap water must be treated appropriately in order to be used as feed water for the sterilization chamber and/or the accompanying steam generator in technical systems.

The necessary water quality is specified in the relevant standards, with the DIN EN 285 standard being currently applicable to the area of water quality for sterilizers (see Table B1). In practice, tap water is treated (for actual desalination / demineralisation) by

means of a single mixed-bed ion exchange and/or in systems involving membrane techniques (reverse osmosis). In some instances, additional electrochemical post-demineralisation processes may also be used. In each case, the goal is to reduce the ion or mineral content of the tap water in a targeted and controlled manner, with the specific conductance of the water usually being used as a significant indicator of the water quality.

Table B1 – Contamination in the feed water for a connected steam generator

Substance/Property	Feed water
Evaporation residue	≤ 10 mg/l
Silicate	≤ 1 mg/l
Iron	≤ 0,2 mg/l
Cadmium ^a	≤ 0,005 mg/l
Lead ^a	≤ 0,05 mg/l
Heavy metal residues (not including iron, cadmium, lead)	≤ 0,1 mg/l
Chloride ^b	≤ 0,5 mg/l
Phosphate	≤ 0,5 mg/l
Conductance (at 20 °C) ^c	≤ 5 µS/cm
pH (at 20 °C)	5 bis 7,5
Appearance	Colourless, clear, without deposits
Hardness (Σ of alkaline earth ions)	≤ 0,02 mmol/l

Notes: Compliance with these values can be verified using recognised analytical methods.

^a These limits correspond to the requirements for drinking water.
^b The maximum chloride concentration in the feed water influences corrosion in combination with high temperatures.
^c See European Pharmacopoeia

Translation of excerpt from DIN EN 285 published by Beuth Verlag Berlin, see also References on p. 37

1.1 Water constituents and treatment

Though one will occasionally encounter references to 'deionised water' in practice in the context of technical water treatment for steam generation, it should be noted that 'deionised water' is not a defined normative term. In the binding Ph. Eur. and USP compendiums, 'deionised water' is defined as 'aqua purificata'. As a result, each individual is free to interpret the meaning of the terms 'deionised water' or 'partially deionised water' for his/her own field of activity. From a technical standpoint, this state of affairs is highly unsatisfactory, especially when one considers that it would appear to be extremely important to have on hand at all times a precise definition of the standardised water quality required for specific applications, and also to be able to take the appropriate steps to monitor compliance with the required/defined quality limits for the water constituents.

Particularly where the use of mixed-bed ion exchanges in water treatment is concerned, both a continuous monitoring of the specific electrical conductance of the demineralised water and testing for the silicic acid content in treated water are important, since the latter (or in analytically correct terms, the silicate content) is not covered by the typical measurement for specific electrical conductance.

A required—and achieved—specific electrical conductance value of 5 $\mu\text{S}/\text{cm}$ therefore does not automatically equal a permissible silicate content (of less than 1 mg/l). The amount of silicate or silicic acid can only be determined using chemical methods, not by measuring electrical conductance. Specifically where standardised mixed-bed ion exchanges are used, one encounters the reoccurring problem of the silicic acid / silicates breaking through the ion exchanges. This is why the silicic acid / silicate concentrations which are ultimately present in the treated water are frequently cited as being the (partial) cause of the formation of yellowish-brown to violet-blue discolourations found on stainless steel surfaces.

Additional information is available from the Red Brochure published by the German Instrument Reprocessing Workgroup AKI ('Instrument Reprocessing, Reprocessing of Instruments to Retain Value') at www.a-k-i.org.

Another element that can in some cases be found in inadmissibly high concentrations in treated water following an incomplete or improper water treatment process (e.g. during water softening) are chloride ions. Even where small amounts on the ppm scale are present as the stainless steel surface dries

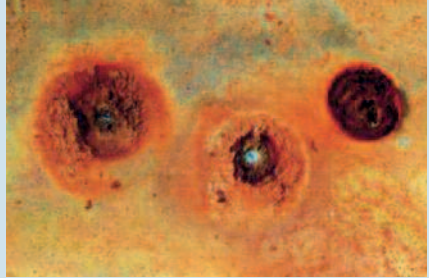


Figure 3: Chloride-induced pitting (source: AKI)

following the sterilization process, this is enough to cause a critical accumulation on the surfaces. At low chloride concentrations, austenitic stainless steel alloys with low pitting resistance equivalent numbers in particular, such as 1.4301, 1.4404, 1.4571 or other similar alloys, exhibit a susceptibility to what is known as chloride-induced (local) pitting and to stress corrosion cracking.

Another important factor for water treatment is the actual oxygen content in the water. At room temperature, natural water will always contain a certain amount of dissolved atmospheric oxygen. This oxygen content can be greatly reduced by the processes applied during water treatment – in particular, through heating.

However, because oxygen—in addition to other conditions—is critical to the formation of passive layers and also in regard to maintaining these layers on stainless steel surfa-

ces, the aspect of oxygen availability is extremely important for any other considerations. (see also Chapter 2)

Disruptions in the passive layer, which is rich in chromium oxide, inevitably cause the material to lose its chemically inert surface properties and, as a direct result, lead to the possible appearance of corrosion effects under critical environmental conditions.

1.2 Consequences of inadequate water treatment

The consequences of incomplete or inadequate water treatment in the case of feed water for sterilization steam can thus sometimes be visually recognised in various system locations immediately following sterilization. For this reason, it is particularly important to regularly test the water quality.

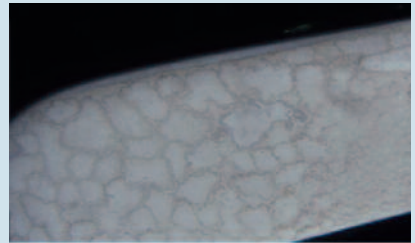


Figure 4: Salt residues (source: Miele)

2. Stainless steel – a brief lesson in materials science

In addition to the main alloying element iron (Fe content normally > 50%), non-corroding (rust-resistant) iron-based stainless steel alloys also contain additives from various alloying elements such as chromium, nickel, manganese and, in some cases, molybdenum, etc. for the following purposes:

- ➔ To obtain the desired performance characteristics (for example, corrosion-resistance)
- ➔ To ensure the desired working properties
- ➔ To provide specific physical properties, such as strength and hardness

The technical literature in this field describes a vast number of available iron-based stainless steel alloys along with the different alloying elements in the alloy composition specified by DIN EN standards such as 10020, 10027-1 and -2, 10028, and 10088-1, -2 and -3.

The term 'stainless steel alloy' will be used throughout the text below to generally denote all non-corroding stainless steel such as 1.4301, 1.4404 and other similar steels. Generally, a distinction is made between austenitic, ferritic, martensitic and ferritic-martensitic duplex alloys. The alloys are distinguished, among other things, by their different levels of corrosion resistance.

In the medical and pharmaceutical fields, different types of stainless steel alloys are used depending on the specific purpose.

For example, because of the special hardness requirements involved, most surgical and dental instruments are made from martensitic stainless steel alloys.

However, compared to austenitic stainless steel alloys, martensitic alloys attain much higher hardness values following the hardening process and, when subjected to the right mechanical working, a consistent sharpness.

Implants and device components that are exposed to significant mechanical pressure loads during use, for example, are preferably manufactured from different variants across the range of available austenitic stainless steels. From a production standpoint, these alloys are usually less expensive to process than ferritic or martensitic stainless steel alloys.

Without a doubt, the typical and probably most important performance characteristic of stainless steel alloys is their corrosion resistance. This chemical property can be attributed to the unimpeded presence of a full-area, homogeneous and firmly adhering passive layer that is rich in chromium oxide.

From a chemical and thermodynamic perspective, the passive layer is what is responsible for corrosion-protected and chemically largely inert stainless steel surfaces.

The chemical element chromium is critical to the formation of the passive layer, since chromium(III) oxide (Cr_2O_3) is the main constituent of an intact passive layer aside from Fe and Fe oxide.

The protective passive layer of a stainless steel surface forms when the element chromium (as a major statistical constituent of the stainless steel surface) combines with oxygen, e.g. from the air, from aqueous solutions with physically dissolved oxygen, or from other oxygen-providing passivation solutions, and creates on the stainless steel surface a layer that is consistently rich in chromium oxide. Despite an extremely low thickness of just 13 nm (equal to roughly 5–10 atomic layers), this layer is capable of forming a chemically protective (inert) barrier between the metal and the surrounding environment whilst allowing electrons—but not ions—to pass, and thus constantly blocking potential corrosion currents at the component's surface.

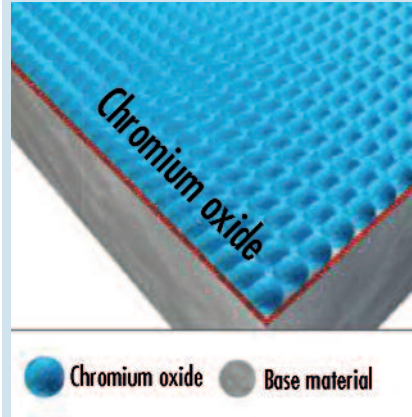
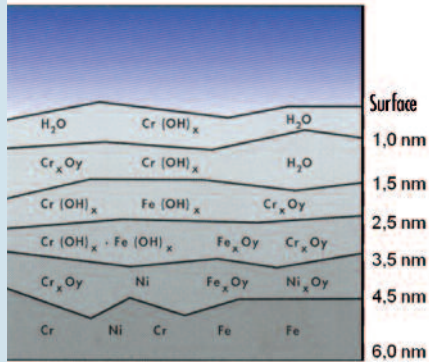


Figure 5: Model depiction of an intact passive layer [1], [2]

Chemically, the passive layer is composed mainly of chromium oxide as a matrix with incorporations of iron (Fe) and iron (Fe) oxide and nickel (Ni) and nickel (Ni) oxide. Analytical AUGER and ESCA studies of passive stainless steel surfaces show Cr/Fe ratios > 1 , whereas Cr/Fe ratios < 0.3 are usually found in the 'alloy interior' based on the alloy composition.

The corrosion-resistant material behaviour of a stainless steel alloy is generally the result of its capability to form the 'chromium-oxide-rich passive layer', which converts the component's surface into a 'passive',



Basic structure of the metallic surface matrix

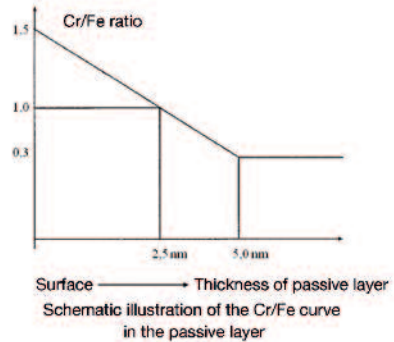


Figure 6: Passive layer thickness / Cr to Fe ratio [5]

non-corroding or extremely inert state. In each individual case, the chemical/thermodynamic passivity of non-corroding stainless steel alloys means that material attack (corrosion) is avoided even under environmental conditions that are predominantly corrosive.

To this, however, it must also be added that

- each individual stainless steel alloy has a different potential corrosion resistance, and that 'higher grade or higher alloy' materials in particular are also resistant to more severe corrosion attacks that would otherwise cause corrosion failure in simpler stainless steel alloys,

and that

- successful passivation requires, among other things, that the stainless steel surface in question also be pre-conditioned such that it is fully capable of being passivated.

2.1 Rouging, a form of (uniform corrosion)

Corrosion can basically be referred to as an undesired, thermodynamically induced, chemical alteration of the surface of a component (in this case: one made of a stainless steel alloy).

In stainless steel alloying technology, a wide range of different local and uniform corrosive effects, resulting from various different causes and mechanisms having more or less serious consequences for the component, is known.

In the case of rouging effects on a stainless steel surface, the phenomenon is a massive alteration in, serious damage to, or even inversion of the chromium-oxide-rich passive layer due to the influence of oxygen-deficient ultrapure water at temperatures $> 60\text{ }^{\circ}\text{C}$, or ultrapure steam. These changes then result in a predominantly iron oxide rouging layer, which can be partially wiped away. The uniform corrosion process described above is referred to as 'rouging' in the related technical literature, which is a term derived from the reddish (Feoxide-rich) material particles that can usually be wiped away.

Technically speaking, rouging describes the typical golden-yellow to reddish-brown formation of film/discolouration on stainless steel surfaces with long-term exposure to hot, oxygen-deficient, salt-free water.

In clean-steam systems with high temperatures ($T > 100\text{ }^{\circ}\text{C}$), it is even possible to observe rouging effects in the form of dark brown to violet films that normally stubbornly adhere to the surface. Relevant material analyses have shown that the rouge film formed on the stainless steel surface is essentially composed of heavy metal oxide particles (e.g. iron, chromium, nickel, etc.), with the iron oxide content clearly being predominant. As a result, it is safe to assume that—both with regard to their type and their relation to the composition—rouging deposits are a corrosion product of the specific stainless steel alloy.

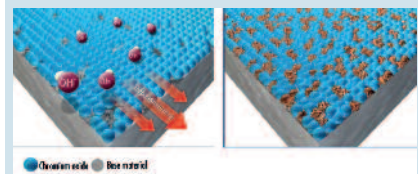


Figure 7: Formation of a rouge layer [1], [2]

From a thermodynamic standpoint, the chemical process behind the entire rouging process is thus an advanced state of oxidation of the stainless steel material, or of its metal atoms, directly on the surface that has come into contact with media, a state that goes well beyond a passivation reaction.

In combination with pure, oxygen-deficient water or clean steam as environmental conditions for austenitic stainless steel surfaces in qualities of 1.4301/1.4404/1.4435/1.4571 etc., high process temperatures (> 60 °C) have clear negative effects on the morphological structure or natural repassivation property of stainless steel surfaces (= self-regeneration of the passive-layer conditions).

In addition to the oxygen depletion in the water, high water temperatures of up to 100 °C also cause an additional decomposition (dissociation) of water molecules accompanied by the formation of H⁺ and OH⁻ ions. As a result of the increased formation of iron hydroxide, this in turn has a negative influence on the stability of the passive layer. At the same time, the oxygen deficiency causes not only a depassivation, but also prevents any further adequate repassivation (= oxidation of chromium), whereby a critical shift in the dynamic balance of de- and repassivation occurs, with this ba-

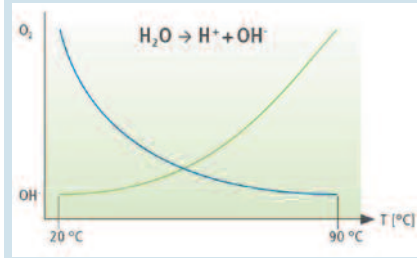


Figure 8: Decomposition of water molecules as temperature increases
Blue curve: Decrease in oxygen content
Green curve: Increase in water decomposition (formation of ions) [1].

lance clearly tipping towards depassivation.

Taken together, this leads to a noticeable reduction in the passive layer's effectiveness and, over time, ultimately to the formation of the predominately iron oxide rouging layer, due to the systematic breakdown/decomposition of the closed protective chromium oxide layer. In the process, the impact of the iron-dominated base material is magnified. In terms of potential, these changes essentially amount to an initially local and eventually complete depassivation.

Due to its bonding energies, iron exhibits—particularly at higher temperatures—a higher affinity for the free hydroxide ions (of the water) that are present as a result of the temperature-induced increased decomposition of the water. More iron hydroxide forms on

the activated stainless steel surface as a precursor of the iron(II) and iron(III) oxide.

In a thermodynamically induced phase inversion, the predominantly chromium oxide protective layer, which was initially present as a passive surface, is converted into a layer rich in iron oxide. This new iron oxide layer (= rouging layer) forms a cover which has a microporous, layered structure that is typical of rusty steel surfaces. The mechanism behind the production/formation of rouging is essentially a form of uniform corrosion. In many cases, no distinction can be made between the corrosion products of rouging and the uniform corrosion due to completely different mechanisms.

Compared to other types of corrosion, typical rouging is relatively easy to identify, usually by means of a simple swab test (see Figure 9).

In many application cases—especially in steam sterilizers—the occurrence of typical rouging films on the component surface, and the accompanying significant discolouration, cannot be avoided due to the combination of high water or water vapour temperatures, oxygen deficiency and the (thermodynamic) property of the specific material (= defined stainless steel alloy).

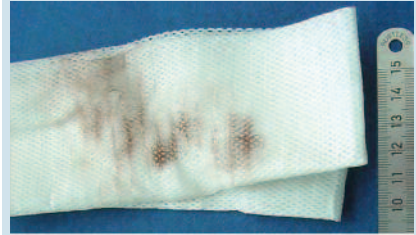


Figure 9: Swab sample from a stainless steel surface covered by rouging [6]

In light of these circumstances, operators need to specify preventative and restorative measures in order to create corrosion-resistant passive surface conditions.

3. Cleaning and maintaining the chamber

3.1 Cleaning residues

When cleaning a sterilization chamber, it is important to follow the user manual and maintenance instructions provided by the manufacturer of the specific sterilizer.

Cleaning agents and methods that are not explicitly recommended or approved by the sterilizer's manufacturer should not be used.

The reason for this is that, among other things, complex interactions which may damage the individual sterilizer, its fittings or its peripheral equipment, can occur during the surface-cleaning process.

3.2 Regular chamber maintenance

Practical experience has shown that, on chemically or electrochemically cleaned bare metal interior surface regions of sterilizers, undesirable surface discolourations/films can be significantly inhibited, or even prevented, by wiping out a cold chamber on a weekly bases with water that meets the specifications of DIN EN 285 (feed water), without adding any cleaning agents.

Any residues stubbornly adhering to the interior surface of the chamber (e.g. from labels, etc.) must be manually removed as soon as possible with the use of appropriate

scraping tools (plastic scraper or other similar items, do not use metal tools). However, when doing so, one must take care not to damage (scratching or other forms of damage) the chamber's interior surface.

The use of chemical substances to remove residues on the interior surface of the chamber should first be approved by the chamber's manufacturer.

Once any films that can easily be wiped away are removed from the chamber's interior surfaces, the stainless steel surface can also be selectively repassivated as part of regular chamber maintenance. This can be carried out in an accurate and reliable manner with the use of wet-chemical acidic passivation solutions. Depending on the specific manufacturer, different aqueous solutions offer the optimal combination of surface care and repassivation capacity.

4. Removing rouging films or corrosion products

Among the specialists directly impacted by this phenomenon (equipment manufacturers and users), there is presently a wide range of different opinions on the cause, resulting problems and recurring need for restoration related to films in sterilization chambers.

A number of those involved describe these films mainly as 'merely visually bothersome', whilst others demand a periodic residue-free removal. The marked difference in attitude towards these issues makes it clear just how controversial the phenomenon is among experts today.

For the purposes of practical application, this means that, with the aid of a risk analysis, every responsible central sterile services department (MPPU/CSSD) must ultimately decide on its own short- and medium-term policy for its immediate sphere of influence.

If a department decides to implement periodic mechanical, chemical or electrochemical restorative measures, it has an array of different options to choose from – all of which, however, must be performed by specialist companies in cooperation with both the equipment manufacturer and the user.

All measures require the following:

- ➔ The operator, sterilizer manufacturer and rehabilitation company specialising in sensitive stainless steel surfaces must all work together
- ➔ Fittings must be removed and treated separately
- ➔ Occupational-safety measures must be planned and adhered to
- ➔ Operator must account for sterilizer downtime
- ➔ Where applicable, dust protection walls must be put up and certain operator-specific safety precautions taken
- ➔ Quality control, including documentation of rehabilitation measures, must be carried out

Figures 10 and 11 in this brochure are intended to illustrate the necessary work involved in the on-site removal of surface films in sterilization chambers.

In general, different options or combinations of techniques are available for effectively removing surface films. These options should always be decided on in consultation with all of parties involved. These decisions should take into account both the severity of the rouging film and, above all, the local conditions.

Mechanical removal



Creating a work area (dust protection wall)
(source: Henkel Beiz- und Elektropoliertechnik)



Figure 11: Quality assurance (surface roughness measurement on the chamber's interior surface)
(source: Henkel Beiz- und Elektropoliertechnik)

If a chamber's interior surface has been severely discoloured by rouging, the affected regions can be cleaned-up for a more slightly appearance by performing a thorough mechanical cleaning (using abrasive mechanical processes).

It should be kept in mind that, during this technical procedure, a significant portion of the iron-oxide-rich particles will inevitably be compacted into the stainless steel surface and thus stored there, which means that corrosion is bound to form again in the near future as the apparatus continues to be used. In most cases, the rouging/corrosion film thus reappears before long.

For this reason, a purely mechanical surface rehabilitation should be viewed in an critical light.

In some cases, stubborn soiling also occurs, e.g. from adhesive labels which can be well and truly baked onto the surface at the temperatures used in sterilization. Aside from soaking the affected area in water or chemical solvents and then using plastic spatulas for removal, there is no other alternative to a mechanical cleaning in these situations. When soiling of this type occurs, mechanical cleaning is also necessary as a pre-treatment for other chemical or electrolytic treatment options that may be used.

The main difference to (very simple) regular care/cleaning with water that meets the specifications of DIN EN 285 (feed water) is that suitable stainless steel cleaners (containing no chloride!) are used, and that rougher fiber fleeces are used in place of cotton cloths. Cleaning can also be performed by machines (e.g. brush-sanding or polishing machines). To do so, (sanding/polishing) cloths or belts are fit onto the machines to facilitate the mechanical removal of the films. However, this does not minimise the basic technical caveats that apply to mechanical cleaning methods.



Figure 12a: Mechanical rehabilitation measures (source: MMM)



Figure 12b: Mechanical rehabilitation measures (source: MMM)

Particularly where surfaces are to be mechanically sanded/polished or electropolished, the procedure used to perform mechanical rehabilitation must be carefully considered or adapted, as the condition of the surface (e.g. surface roughness) can be deteriorated as a result. When the interior surfaces of a chamber are electropolished, mechanical processes—including the use of fibre fleece materials or even brush-sanding/polishing measures—have an adverse effect, at least locally, on the stainless steel surfaces.

A thorough cleaning will usually destroy the passive layer. Waiting for a certain amount of time (normally about 48 hours) whilst also allowing air to freely enter the chamber is therefore recommended before putting the system back into operation, so as to allow the passive layer to regenerate (natural

repassivation). Active (wet-chemical) passivating agents can also be used to optimise and greatly speed up the repassivation process. This approach also improves the passive layer's chemical characteristics (e.g. thickness, Cr/Fe ratio).

However, it is important to keep in mind that this mechanical grinding of stainless steel surfaces causes a permanent destruction of the passive layer. Experience has shown that this then eliminates the possibility of a complete natural self-regeneration of the passive layer, or even a regeneration that is equivalent to the results seen on electropolished surfaces. This means that a natural air-based repassivation will take place either to a limited extent or not at all, since stainless steel surfaces that have been structurally altered (damaged) by mechanical processes no longer possess their full passivation capacity. In these situations, however, wet-chemical repassivation agents can be used to at least promote a repassivation.

Once the mechanical cleaning is complete, it is important to ensure that all residues (e.g. dust and any sanding/polishing materials) are completely removed.

4.2 Methods of chemical removal

There are different options available for chemical removal, each of which will be described below.

These options can be used separately or, where necessary, in combination with one another.

4.2.1 Chemical pickling

Pickling is an intensive chemical treatment of stainless steel surfaces that is reserved for specialist companies. One of the benefits of this method is that it can dissolve even smaller-scale inorganic impurities and systematically clean them off of surfaces. As a rule, all pickling agents cause a minimum amount of material abrasion (from 1 to 3 μm) during the cleaning process. The chemicals used for this purpose are typically based on hydrofluoric acid and nitric acid in aqueous solution, and are available in the form of baths, pastes and sprays. The acids essentially react in the following two-stage process:

- ➔ (1) Metal oxidation, and
- ➔ (2) Dissolution of the metal oxide / reaction forming metal fluoride as a typical metallic salt

Before the pickling process can be applied, anything covering the surface (e.g., adhe-

sive labels) must be removed to ensure that the treatment chemicals can reach the surface at the same time without any hindrances.

Selecting the proper pickling agent and the appropriate pickling method, as well as the correct parameters, depends on various different criteria:

- ➔ Which type of stainless steel or grade of alloy is being pickled?
- ➔ How extensive are the films that are to be removed?
- ➔ Which surface requirements (e.g. final roughness Ra/Rz in accordance with DIN EN 4288) will the pickled component be subject to?

Depending on the pickling agent used / pickling parameters selected, the stainless steel surface will have a fully passivable surface after the pickling, activating and rinsing. For a spontaneous formation of a protective passive layer, a suitable chemical passivation step is subsequently recommended, after which the surface should be rinsed with water that meets the specifications of DIN EN 285 (feed water) to achieve a final acid-free (pH of 7) state. The passive layers that can be expected normally exhibit an average thickness of approx. 1–3 nm. Oxidising media (e.g. nitric acid or hydrogen peroxide) are effective passivating agents.

4.2.2 Chemical derouging

The wet-chemical passivation takes place within a span of a few seconds to a few minutes.

Suitable complexing agents (NTA, EDTA, GLDA, citric acid)—normally used as an additive in wet-chemical passivation solutions—can also be used for post-treatment to remove any iron ions present on the surface. However, these substances do not have a re-passivating effect on stainless steel surfaces, though it should be added that when aqueous nitric acid is used in activation after pickling, a corresponding synthesis of passivation effects and final cleaning is achieved.

Where chemical products are used for pickling, activation, passivation and also for degreasing beforehand, the safety data sheets and processing information provided by the manufacturer should be observed for each product.

The complex processes involved in pickling underscore the importance of the need for this type of work to be performed solely by a specialist. This is necessary to ensure that permanent damage to equipment and its surfaces is prevented (e.g. what is referred to as 'overpickling').

In chemical derouging that involves the use of a predominantly organic complexing agent solution, films such as heavy metal oxide particles (of iron, chromium, nickel, etc.) located on or adhering to stainless steel surfaces are chemically cleaned off of the surfaces without leaving behind any residues, and without attacking or damaging the stainless steel surfaces. This is an important and, in the case of complex component geometries, often decisive process advantage over chemical pickling, which means that chemical derouging delivers much greater process reliability.

The chemical treatment takes place in a closed chamber by means of a controlled wetting of the chamber's interior surfaces with cleaning solutions kept at controlled temperatures. In principle, it is also possible to completely fill a fully sealed chamber with a suitable cleaning fluid, and to carry out the cleaning programme over a predetermined application time. As an alternative, an effective cleaning can also be successfully carried out using a relatively small amount of fluid by circulating the solution through suitable pumps and spray heads in the chamber area.

Following the actual cleaning step (= derouging procedure), the affected chamber surfaces are re-passivated using special passivation solutions and are then rinsed

with water that meets the specifications of DIN EN 285 (feed water) to remove all remaining acid. After this last step, an electrical conductance measurement is used to check the effectiveness of the acid removal.

By choosing derouging solutions that are chemically and environmentally much gentler, this purely chemical treatment—unlike chemical pickling—eliminates surface attacks and deterioration of the surface roughness, even with longer application times, since the chemical resistance of the stainless steel alloys involved is not decreased in the derouging solutions.

With the appropriate care and thorough preliminary planning/preparation/organisation in collaboration with the system operator, apparatus manufacturer and an experienced derouging specialist, steam sterilizers can generally be chemically derouged on-site without any problems.

4.3 Electrochemical (anodic) cleaning

Electrochemical (anodic) cleaning of stainless steel surfaces contaminated with rouging is based on the concept of electropolishing.

As a reversal of the electroplating process, electropolishing uses a suitable electrolyte and an application of direct current to remove material (metal atoms) on the μm scale from a workpiece surface, which serves as the anode, by means of electrolytic metal oxidation.

Electrochemical removal processes can be applied successfully and reproducibly in both an immersion bath method and in a suitable wiping technique (as a mobile version). The qualitative surface conditions of stainless steel chambers in terms of corrosion behaviour and cleanability are significantly improved in these controlled electrochemical treatments.

Before any specific on-site cleaning measures are actually carried out, the equipment operator, equipment manufacturer and the technicians from the electropolishing specialist come together in an engineering meeting to plan the technical, safety-related and organisational procedure and discuss the necessary preparations.

Operator representatives in charge of work

safety and hygiene are also involved in the preparations, and are given the necessary data and information by the electropolishing specialist.

Because all of the work that needs to be performed is completely isolated by film enclosures installed ahead of time (see Figure 13), this measure can be carried out on a sterilization chamber without interrupting MPPU/CSSD operations, and a full continued supply of sterile goods can be ensured using the other devices.

Electrochemical cleaning involves a controlled wetting of the interior surfaces with a suitable electrolyte using a mobile hand tamping unit in combination with a fleece body and an embedded cathode. In the designated working area of the chamber surface serving as the anode, a time-dependant targeted removal of material from the surface takes place on the scale of 5–10 μm in a controlled electrical anode/cathode field by means of electrochemical oxidation (= electropolishing).



Figure 13a:
On-site rehabilitation of an interior surface on a chamber
using electrochemical (anodic) cleaning
(source: Henkel Beiz- und Elektropoliertechnik)



Figure 13b: Workspace partitioning
(source: Henkel Beiz- und Elektropoliertechnik)

The electropolishing process ensures that all films or residues are carefully removed from the stainless steel surface without leaving behind any residues. In addition, and virtually at the same time as the targeted electrochemical material removal, a micro-smoothing of the surface (reduction of surface roughness) also takes place. As a result of this, and depending on the material characteristics (of the original surface), one can usually expect to see a significant improvement in surface quality with regard to corrosion-resistance.

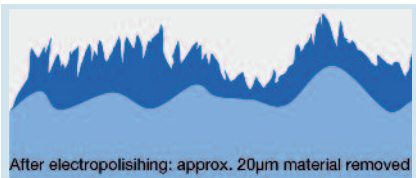
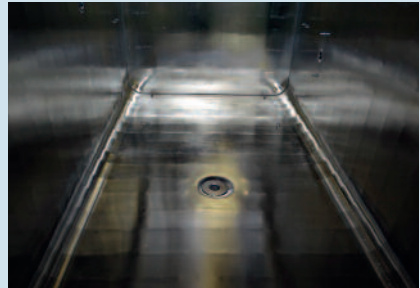
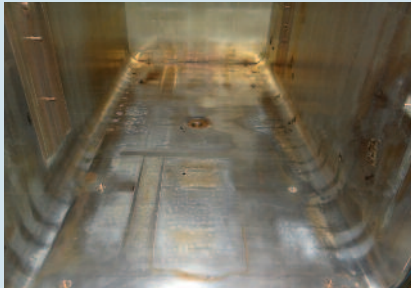


Figure 14: Schematic illustration of the surface contour before (dark blue topography) and after (light blue topography) [4]

After the applied electrochemical material removal and the resulting residue-free cleaning of the stainless steel surface, a rinsing step is subsequently carried out with water that meets the specifications of DIN EN 285 (feed water). In the work step that then follows, the passive layer is built up by means of wet-chemical passivation. In a final step involving a thorough rinsing of the chamber with water that meets DIN EN 285 specifications (feed water) and the measurement of electrical conductance to monitor the rinsing progress, all remaining traces of the cleaning solution are safely and verifiably removed.

Throughout the entire procedure, all treatment parameters, such as surface roughness before and after cleaning, temperatures, pH and electrical conductance of the solutions, are documented in detail. Once the apparatus has been functionally re-qualified by the equipment manufacturer, the steam sterilizer can be completely handed over to the customer for use again after a total treatment time of approx. 1–2 days.



Figures 15a and 15b: Steam sterilizer before (left) and after electrochemical (anodic) cleaning (right)
(source: Henkel Beiz- und Elektropolieretechnik)

Following completion of the electrochemical cleaning, the chamber's interior surfaces exhibit homogeneous surface conditions with microscopically smooth, reflective/glossy properties. In addition, the surface smoothing which has taken place on a microscopic scale (massive reduction in actual surface area) results in significantly improved corrosion properties and better cleaning behaviour for any new films and discolourations that form in the future.

Electrochemical cleaning also optimises and simplifies the subsequent regular care of a chamber's interior surface.

5. Summary

In light of the large number of influencing parameters and the resulting complex interrelations, and because of the parallel effects of different influencing factors, individuals in charge of sanitizing equipment often find it very difficult in practice to determine the specific cause that has actually led to an (undesired or bothersome) alteration of the stainless steel surfaces located in the interior of a chamber.

The aim of this brochure is to describe and identify the phenomenon known as rouging as a change in the surfaces of sterilizer chambers. Measures which have already been successfully implemented in practice are also described. In all of the methods covered, an active and focused collaboration between equipment users, the equipment manufacturer and the specialist cleaning company is a constant requirement.

Begriffserklärungen und Abkürzungen

A

AKI

German Instrument Reprocessing Workgroup

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Activation

Use of acids to remove oxide impurities on surfaces.

AUGER

Spectroscopic analytical technique used in the non-destructive study of material surfaces to determine their chemical composition.

Austenitic

A stainless steel alloy in which the metal atoms have a face-centred cubic arrangement in the ordered metal lattice system.

The individual system is established when the molten material solidifies, with the unit crystals always growing in different directional orientations.

C

Cl =Chloride, ions of the element chlorine

Corrosion

Term referring to changes occurring on the surface of a material as part of an (undesired) chemical reaction. In serious cases, this can essentially result in the destruction of the material/component.

Cr = the element chromium

CSSD = central sterile services department, new term MPPU

D

Deionised water

Term from the field of water treatment. Level of water quality that is not standardised. Deionised water typically refers to product water with an electrical conductance of less than 5 $\mu\text{S}/\text{cm}$ following ion exchange demineralisation.

E

EDX

Energy dispersive X-ray analysis as a method of chemical analysis.

ESCA

Electron spectroscopy for chemical analysis.

EDTA

Ethylenediamine tetraacetic acid or ethylenediamine tetraacetate Forms metal complexes which then exhibit the desired effect. Used to dissolve residues on surfaces.

F

Ferritic

Stainless steel alloy with a body-centred cubic metal atom arrangement in the ordered metal lattice.

Fe = the element iron

G

GLDA = tetrasodium glutamate diacetate
Complexing agents, also known as chelating agents, are chemical compounds which form chelate complexes with metal ions. They result in a masking (bonding) of undesired metal ions (iron ions).

M

Mixed-bed ion exchange
Mixture of cation and anion exchange resin. This mixture removes all salts (mineral, dissociated water constituents) from the water as it passes through the ion exchange.

Martensitic

Crystalline structure of an alloy that consistently occurs during hardening. The metal atom arrangement in the accompanying metal crystal lattice is usually tetrahedral.

Morphological structure

Description of the precise configuration of the alloying elements on the surface of the stainless steel alloy.

MPPU

Medical products processing unit

N

NTA

Nitritotriacetic acid

Chemical used for treating/cleaning stainless steel surfaces. A metal complexing agent.

Ni = the element nickel

O

Oxidation

Generally speaking, oxidation is essentially any chemical reaction in which an increase in valence occurs, and is also a chemical process involving oxygen, usually in connection with damage to / destruction of a surface and rust formation.

P

Ph. EUR

European Pharmacopoeia
(Europäische Pharmakopöe)

Pitting

A specific (local) type of corrosion, usually caused by chloride ions.

R

Ra = Arithmetical mean roughness value, a surface roughness parameter according to DIN EN ISO 4287

Rz = Mean roughness depth, a surface roughness parameter according to DIN EN ISO 4287

Rouge, Rouging

Originally a French term used to denote the application of red make-up hues. Used in this context to refer to the reddish-brown films/dicolourations (corrosion) found in chambers or on chamber surfaces.

S

Silica

Categorical term for water constituents containing silicic acid. These substances can be partially responsible for undesired coloured films.

Silica breakthrough

Denotes the incomplete removal of silica compounds during the use of mixed-bed ion exchanges in the production of treated water.

Steel, non-corroding / stainless steel is a high-grade alloy of iron and other (Cr, Ni, Mo, etc.) elements that meets the specifications of DIN EN 10020, 10027-1/2 and 10088 and will not rust under certain conditions.

U

Ultrapure water

Refers to fully demineralised water which satisfies the requirements for steam sterilization. Not a defined quality concept from any specific standard.

USP

United States Pharmacopeia

W

WD = Washer-disinfectant

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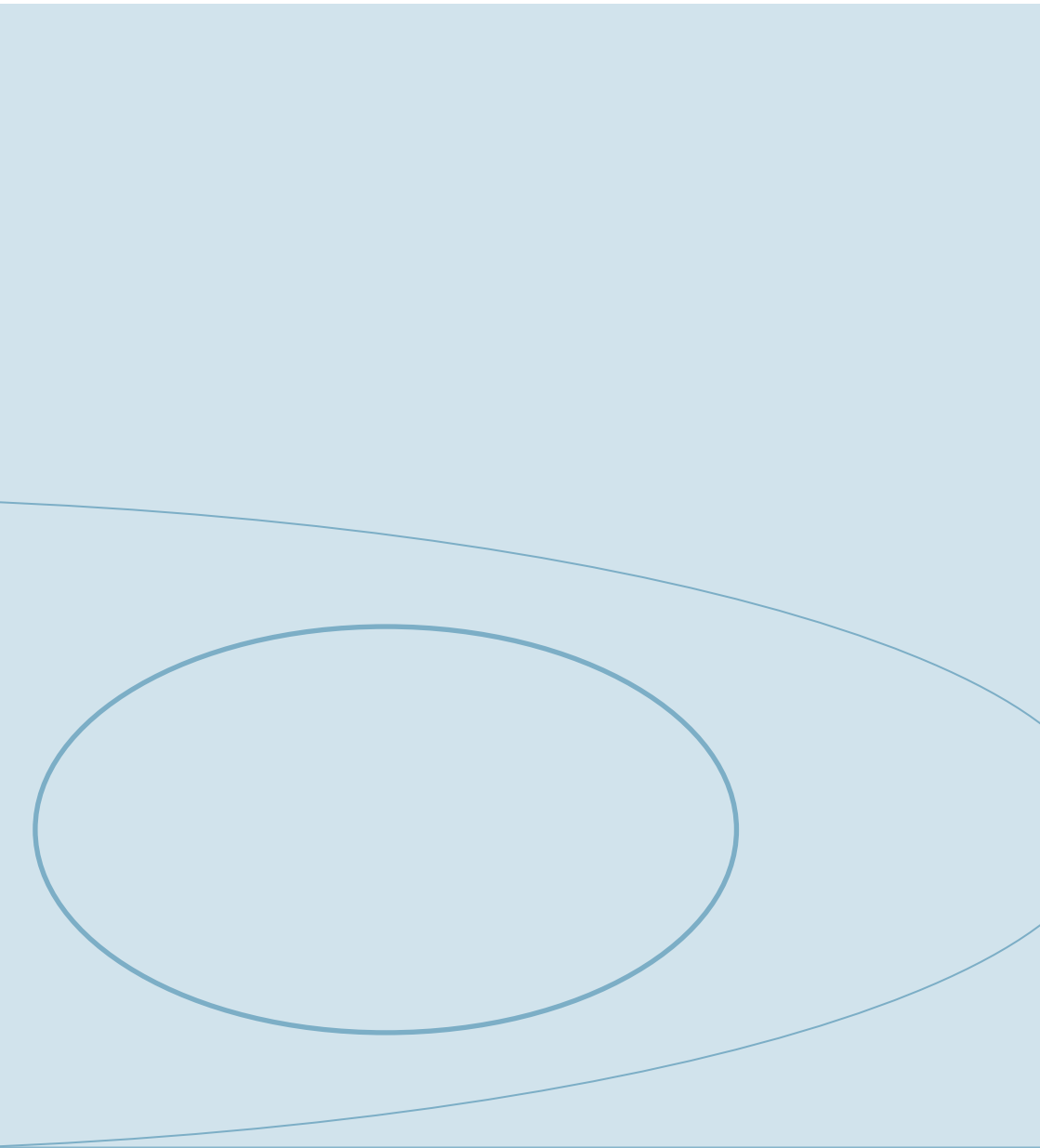
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AKI, Arbeitskreis Instrumentenaufbereitung (German Instrument Reprocessing Workgroup): www.a-k-i.org

DIN Deutsches Institut für Normung e. V. (German Institute for Standardization), Berlin DIN EN 10020, 10027-2, 10029-2, 10088-1, 10088-2, 10088-3, DIN EN 285 The various standards cited in this document can be ordered there.





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