

This article presents the results of an experimental study conducted to support the basic understanding of the rouging phenomenon that often occurs on stainless steel in WFI systems. With the established exposure technique, it is shown that rouging is affected by the surface quality and composition of gas atmosphere.

Using Exposure Tests to Examine Rouging of Stainless Steel

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Introduction

For many years, numerous cases of red-brown to dark violet deposits on the inside surface of distillation columns, storage vessels, and distribution systems for hot purified water and clean steam have been reported. Due to the visual appearance, those deposits were referred to as *rouge*. Rouge was observed in pharmaceutical Water for Injection (WFI) systems, which are typically made of austenitic CrNiMo steel grade AISI 316L. The formation of rouge is promoted by elevated temperatures above 60°C - *Figure 1*.

Since the presence of rouge is not considered as critical for the water quality as required by current pharmacopoeias, it may represent a potential risk of particulate contamination of pharmaceutical product solutions. Therefore, it may necessitate consistent repeated cleaning operations or proper installation of additional filters at the point of use.

A literature survey gained a wide range of opinions as to the origin of rouge, e.g. localized corrosion in vulnerable areas of the passive film,¹⁻⁹ poor welding including heat tint,^{4,8,10,11} and various surface contamination such as mild steel particles,^{2,7} grinding dust and residues from emery wheels.^{7,8,12} Otherwise, the literature is very focused on the various possibilities for "de-rouging" of pharmaceutical water sys-

tems.^{3,5,8,10,13,14} The two most widely used media for de-rouging are acids and chelants.

In 1997, Jessen¹⁵ reported a strong influence of the composition of the gas atmosphere, which is in equilibrium with the boiling water and the vapor phase on the formation of rouge. Whereas carbon dioxide containing and/or oxygen depleted media strengthen the formation of rouge, saturation with oxygen inhibited the phenomenon. These findings were the basis for the initiation of a new research project in 1999. The main purpose of this project was to reproduce some of the interesting results from the earlier Project Rouge I by limiting the number of parameters within each experiment and to determine the influence of different surface treatments and alloys.

Methods

Materials and Preparation

Coupons for exposure tests were produced from 2.0 or 2.5 mm plate material of the stainless steel grades shown in Table A. Each coupon measures 100x100 mm and includes a center hole (Ø12 mm) and a weld. The welding procedure applied (GTAW) ensured a δ -ferrite content of less than 5% for the austenitic grades (316L and 904L), and between 30-70% for the duplex 2205 grade. Both sides of the weld seam were pickled with HF/HNO₃ based paste. Since rouging often is associated with welds that inevitably occur in WFI systems, only welded coupons were included in the exposure tests.

In order to test extreme surface conditions, the coupons were prepared in either the original finish, a ground or electropolished finish. The major characteristics of the tested materials are summarized in Table B. The ground finish was produced using aluminum oxide fiber disks (P80). Electropolishing and follow-up treatment was strictly controlled and performed in concentrated phosphoric/sul-

Figure 1. Rouging on the internal surfaces of a WFI system.⁵



phuric acid solutions at about 50°C according to HE111-processing (material removal approx. 20 µm). The final treatment of all coupons was chemical passivation in 20% HNO₃ for 30 minutes at ambient temperature followed by DI water rinsing.

Exposure

During exposure, the coupons were mounted on a Teflon hosed titanium (Gr.1) rack. Each rack contained 30 coupons separated by Teflon spacers (1.5 mm) while Teflon strips were inserted for every third coupon. Four identical exposure systems were built from Quickfit parts. Each system included two flasks, i.e., a heated cell containing the coupon rack and a reflux flask. A constant water level was maintained by interconnecting the two cells. Each system was filled with WFI (specific electrical conductivity approximately 1µS/cm) to obtain 80% submersion of the coupons giving a total exposed area of 50 dm.² The exposure tests were conducted with the following gas atmospheres:

- synthetic air
- synthetic air with addition of 1% carbon dioxide
- synthetic air without carbon dioxide. CO₂ was removed by bubbling the gas through a sodium hydroxide solution.
- nitrogen 99.999% (Oxygen level <1 ppm)

The systems were thoroughly purged for three days with the selected gas at a flow of 50 ml/min (mass flow controllers) before turning on the heat. Boiling was then maintained for six weeks at constant gas flow of 25 ml/min.

Evaluation

The coupons were regularly inspected visually to identify any rouging during the exposure period. At the end of the test, water samples were taken from each cell and analyzed for dissolved metals by use of Electrothermal Atomic Absorption Spectrometry (ETAAS) or High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICPMS). The exposed coupons were evaluated by their weight-change, visual appearance, and surface morphology. For this purpose, Light Optical Microscopy (LOM) and Scanning Electron Microscopy (SEM) were applied. The deposits collected on the Teflon strips (or coupons) were analyzed by means of X-Ray Fluorescence (XRF).

Results

The experiments have involved two series of exposure tests to study either the effect of different gas atmospheres or different alloy types. In addition to this, both series included different surface conditions of the materials tested.

In the first series of exposure tests, two extreme surface conditions of 316L were tested in four different gas atmospheres. The coupons included a roughly ground surface finish and an electropolished surface finish placed at each end of the rack. The aim of this arrangement was to prove whether different qualities possibly could be combined and distinguished in the same cell.

The first signs of rouge became visible after four days of exposure while only little development was observed during the remaining exposure period. In all cases, rouge was seen as deposits along the water line of the coupons as shown in Figure 2. The most evident rouge formation was seen in the cells purged with nitrogen or air with addition of carbon dioxide. The

two other atmospheres (air and air + CO₂) showed less or no rouge formation. This became clear when the coupons and Teflon strips were studied closely after dismantling the cells - Figure 3.

The visible degree of rouging is connected with an increasing amount of dissolved metals and the metal oxide/hydroxide deposits collected on the strips as shown in Table C. In all cases, the red brown rouge deposit was identified as a ferrous dominated products by using XRF. Deposits analyzed by EDS in an ESEM verified the presence of other alloying elements (Cr, Ni, Mo) and showed only small amounts of carbon (0.9-2.4 wt-%) in comparison to the high amount of iron (30-50 wt-%). It should be mentioned that the same technique revealed the presence of silicon as colorless deposits on the coupons. The glassware is the most likely source for the dissolved silicon since none of the other exposed materials contain considerable amounts of silicon. Microscopic investigation of the surface of

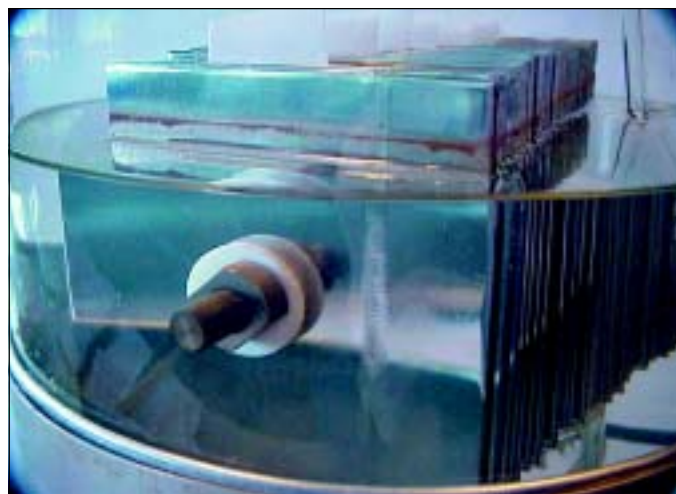


Figure 2. Test cell with a coupon rack showing rouge at the water line after three weeks of exposure in nitrogen purged WFI (boiling was paused). The coupons include both the #80 and the 2B+ep finish of 316L material.

the coupons showed that the rouge product consists of relatively loosely adhered particles - Figure 4. However, since the rouge was evenly distributed on the strips and coupons, the first series of tests did not allow any distinction between the different surface treatments.

Based on these results, the second series of tests were performed separately with each material or surface quality in one cell. In order to produce the most extreme rouging conditions, all tests were performed in nitrogen-purged atmosphere.

From the results in Table D, it clearly appears that the specified and controlled electropolished finish of all alloy types showed less rouging than their untreated counterparts. Furthermore, the untreated finish of the high alloy materials revealed no obvious improvement in performance when compared to the 316L 2B material.

In agreement with the above results, it appears that the metal concentrations are higher in the water samples from the unpolished plates whereas the electropolished counterparts show less dissolved metal - Table D. During the exposure tests, additional water samples were taken after three weeks (316L only). It clearly appears that all coupons release high amounts of iron although the visual rouge formation at that time was limited. Moreover, the iron content is higher than the level of the water samples after six weeks. This difference possibly

Chemical composition of the experimental materials determined by OES ^a (wt-%)										
Material	C	Si	Mn	P	S	Cr	Ni	Mo	N	Cu
316L	0.018	0.51	1.71	0.030	0.002	17.3	12.5	2.6	0.059	0.16
904L	0.014	0.28	1.50	0.021	0.001	19.6	24.2	4.3	0.053	1.43
Duplex 2205	0.022	0.38	1.53	0.022	0.001	22.4	5.7	3.2	0.117	nd.

a) Optical Emission Spectrometry

Table A. Experimental materials.

δ -ferrite content in the weld metal and surface roughness of the tested materials.						
Material	δ -ferrite content in weld metal (Vol-%) ^a		Surface roughness of tested finishes ^b Average Ra (μm) ^c			
Standard steel	Avg.	Min./Max	2B	2B+ep	#80	#80+ep
316L	3.0	1.4 / 4.1	0.22	0.18	1.03	0.39
High alloyed	Avg.	Min./Max.	2E		2E+ep	
904L	not detectable		0.32		0.11	
Duplex 2205	59.1	51.9 / 66.9	0.21		0.10	

a) measured with a Fischer Feritscope M11 and MP3C (both Vol.-% Fe cal.) b) 2B - according to ASTM A480, i.e. skin passed and pickled finish; 2E - annealed, electrolytically pickled, brushed (grit 100) and finally pickled; ep - electropolished finish according to HE111-processing; #80 - ground finish, mesh 80. c) using contact profilometry (Lt 4.8mm/ Lc 0.8mm).

Table B. Characteristics of the tested materials.

may be due to an initial high release rate of iron and subsequent slow deposition. It should be mentioned that silicon from the glassware also was present in the water samples at concentrations that were approximately 1000 times higher than the metal concentrations.

The exposed coupons were further studied under a microscope to identify any signs of corrosion. None of the coupons showed clear indications of corrosion although the electropolished coupons clearly revealed all forms of imperfections or inhomogeneous structures such as small slag particles or weld areas. The ferrite phase in the welds also appeared clearly on the electropolished coupons, but showed no indications of selective dissolution - *Figure 5*. It is more difficult to exclude the possibility of corrosion on the other surfaces since the evaluation was disturbed by either the intergranular etching (2B finish) or grooves (2E finish).

Discussion

The above results show several interesting effects on the formation of rouge on stainless steel in boiling WFI. First of all, the tests consistently show that rouge is an iron rich product consisting of small particles that accumulates preferentially along the water line or on the Teflon parts. This indicates that the particles are formed at the water level and float until they deposit in stagnant areas at the water/gas interface or on Teflon parts due to electrostatic forces. Rouge also was deposited to a lesser degree below the water level at the Teflon spacers, which verifies that the metal dissolution takes place in the water phase. Unfortunately, this behavior implied that different steel qualities could not be tested together.

The first series of exposure tests showed a strong effect of the gas atmosphere composition although the tests allowed no distinction between the two surface conditions in each cell. The most evident rouge formation was observed in the cells purged with nitrogen or air with addition of carbon dioxide, whereas air and carbon dioxide depleted air showed less or no rouge formation. This result indicates a beneficial effect of oxygen and a negative effect of carbon dioxide that respectively may

improve the stability of the passive layer and cause a slight acidification of the media. It should be noted that the final pH was 5.5 of the carbon dioxide containing media whereas the pH in the other media ranged from 7.6 to 8.1. WFI completely purged of all gases was not included in the study, but would probably result in the same behavior as observed for the nitrogen purged experiment, when assuming that the obtained oxygen depleted conditions in both cases have the same effect on the passivation of the stainless steel.

As concerns the effect of surface treatment, the results of the second series of tests show that electropolishing improves the performance when compared with the pickled qualities (2B or 2E). Both surface conditions are regarded as high quality, and all coupons were prepared with great care involving nitric acid passivation as the final treatment. Therefore, it is believed that the improved performance of the electropolished material is related to a marginally higher purity that possibly affects the passive dissolution rate.

The surface finish probably has a very high impact on rouging. Maybe even higher than the individual stainless steel grades. Therefore when comparing the results of the 316L coupons with the more highly alloyed steel types, there is no obvious improvement although the high alloy steel types possess a significantly better corrosion resistance (mainly against chloride and acid attack). One reason for this could be the fact that 316L is tested with a different surface finish than the higher alloyed grades. This could be one of the reasons why the brushed coupons (2E) show at least the same amount of rouge as the 316L coupons and even higher contents of dissolved iron. The electropolishing clearly improves the behavior of the high alloy steel types, and brings the overall performance up to a level of the best 316L coupons. In fact, the content of dissolved iron for the 904L coupons was below the detection limit.

The surprisingly high amount of dissolved iron for the 2E-samples may perhaps be due to a higher passive dissolution rate for the high alloy materials in comparison to 316L. Fundamental work on the passivation of stainless steel in acids shows that an increasing content of molybdenum may

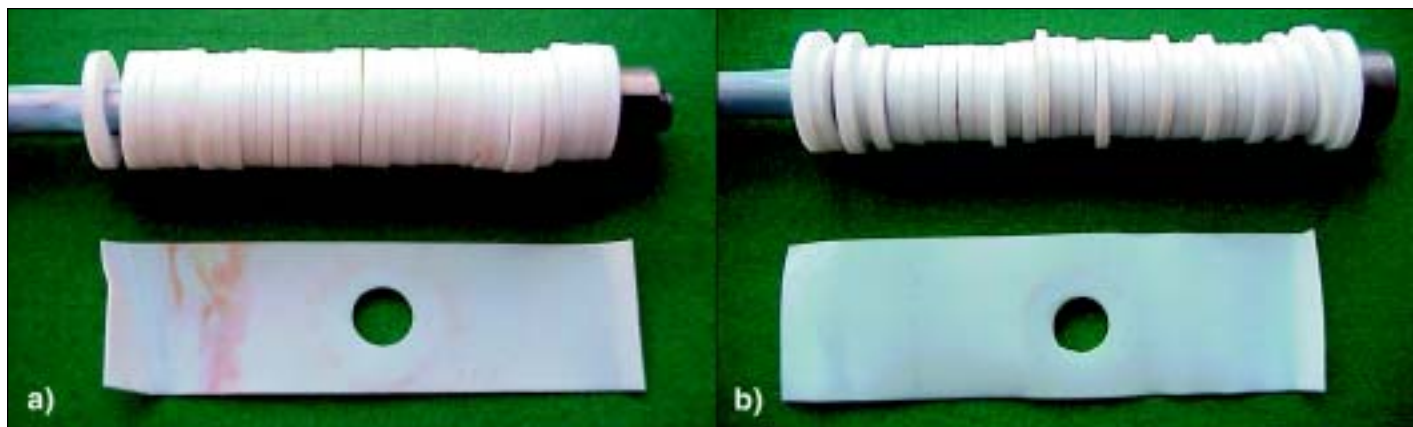


Figure 3. Teflon spacers and strips after exposure of 316L in WFI purged with a) air + 1% CO₂ and b) Air + CO₂.

increase the passive dissolution rate.¹⁶ However, this fact should only be considered as a possibility since the boiling WFI is far less aggressive than the acids used to obtain these data.

The fact that no corrosion was observed on any of the exposed coupons suggests that rouging is the result of slow metal dissolution while the stainless steel remains in its passive state. The possibility of finding any corrosion attack is also weakened by the limited amount of dissolved metals in the water samples.

It is believed that the release of metal (especially iron) is highest during the initial exposure period where the driving force is high due to the low concentration of dissolved metals. Furthermore, the passive oxide film adapts its composition and structure to the surrounding environment during the first

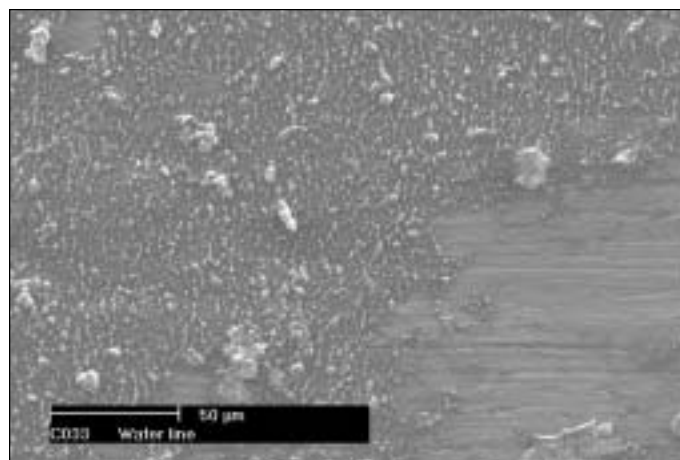


Figure 4. Exposed coupon covered by loosely adhered rouge deposits. Scanning electron micrograph.

hours. This also may contribute to a high initial dissolution rate. The water analysis data and visual observations during exposure support this theory. After a certain period, stationary conditions are probably achieved in the exposure cell as a compromise between the concentration of dissolved metals and the composition of the passive oxide film. This situation differs from the one found in a real WFI system, where the water continuously is consumed and replaced. Therefore, it is considered that the dissolution of metal takes place at a higher rate than indicated by the exposure tests (i.e., less than 20 μg/m²day).

The established experimental technique has, with some success, made it possible to reproduce rouging in the laboratory and thereby study the effects of different parameters. It should

be mentioned that the observed effect of the gas atmosphere previously had been shown using the same exposure technique, but different evaluation methods.¹⁵ Although interesting results were obtained, the established technique is not yet considered perfect due to co-deposition of silicon released from the glassware. This side effect excluded the possibility of correlating the weight-gain of the coupons to the deposition of rouge, and may to some extent also have affected the water chemistry. Moreover, the experimental technique is quite costly since each surface condition had to be tested separately with large number of coupons for a long time to obtain a limited amount of rouge. Efforts are currently being made to refine the above technique and to pursue some of the interesting effects observed in this study.

Conclusion

Long-term tests of partly submerged stainless steel coupons have shown that the rouging phenomenon can be reproduced and studied in the laboratory.

Different surface finishes of 316L steel exposed in boiling WFI purged with different gasses showed that rouging develops faster in atmospheres of carbon dioxide containing air and nitrogen. Purging with atmospheric air resulted in less rouging, while air without carbon dioxide showed no visible rouge formation. The rouge formed was deposited preferentially along the water line or on Teflon parts. The rouge collected was in all cases identified as iron rich deposits. Furthermore, rouging was associated with increased amounts of dissolved metals in the test solution.

Exposure in nitrogen purged WFI of the highly alloyed 904L and 2205 steels in 2E finish showed no obvious improvement in performance when compared to the 316L 2B materials. The electropolished condition improved resistance against rouging and resulted in comparable behavior of the different steel types.

None of the exposed coupons showed any weight-loss or visible signs of localized corrosion. This suggests that rouging is mainly a result of passive dissolution and re-precipitation of metals, mainly iron. It also agrees well with the fact, that rouging may be intensified by any local defect, such as iron contamination, de-alloying or heat tints.

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Summary of results of exposure tests including AISI 316L material tested in WFI at 100°C for 6 weeks. The #80 and 2B+ep surface finishes were tested in the same cell.						
Atmosphere	Dissolved metals, ^a µg/l				XRF-iron intensity on Teflon strips	Appearance of coupons and Teflon strips. Visually assessed
	Fe	Cr	Ni	Mo		
Air	20	0.5	3.8	8.4	Weak	Traces of rouge
Air + 1%CO ₂	39	0.8	23	7.4	Strong	Heavy rouging
Air ÷ CO ₂	23	0.6	6.9	7.4	Weak	No rouging
N ₂	130	1.6	9.0	9.6	Strong	Heavy rouging

a) measured using HR-ICPMS (Fe, Cr, Mo) or ETAAS (Ni).

Table C. Summary of results of the first series of exposure tests.

Summary of results of exposure tests of different alloys tested separately in nitrogen purged WFI at 100°C for 6 weeks.					
Alloy	Surface	Dissolved iron µg/l ^a		XRF-iron intensity on Teflon strips	Appearance of coupons and Teflon strips. Visually assessed
		3 w	6 w		
316L	2B	431	37	Moderate	Distinct rouging
	2B+ep	177	6.8	Weak	No rouging
904L	2E		95	Strong	Distinct rouging
	2E+ep		<2	Moderate	Slight rouging
Duplex 2205	2E		365	Strong	Slight rouging
	2E+ep		59	Weak	Very slight rouging

a) Iron content after 3 and 6 weeks of exposure. The iron content of the WFI was 2.9 µg/l.

Table D. Summary of results of the second series of exposure tests.

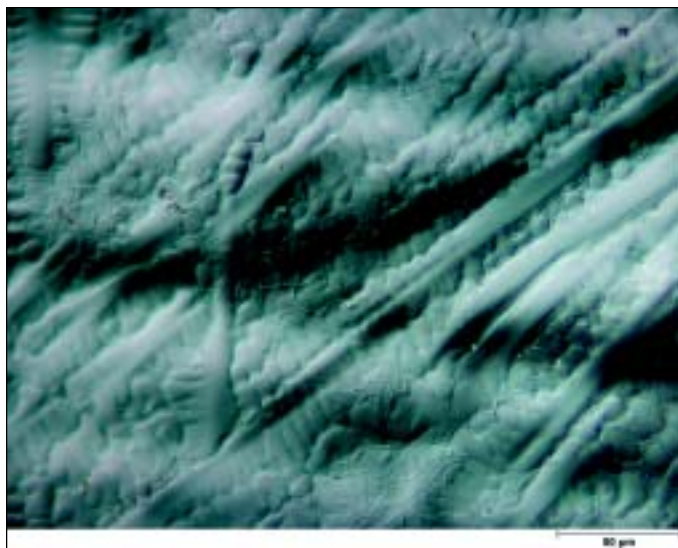


Figure 5. Weld metal of an electropolished 316L coupon. The picture was obtained by light microscopy and shows a small amount of delta ferrite distributed as a skeleton between the primary austenitic phase.

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