ROUGING AND DEROUGING OF STAINLESS STEEL

Unicoat Recover ApS
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Tlf. 42954705

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UNICOAT
Overfladebehandling af rustfrit stål

ateco advanced metal finishing

- Unicoat Recover is part of the coating company Unicoat ApS
- Electric polishing/electrolyte treatment
- Pickling – Dipping/brush/spray
- Passive ring - also of automatic steel
- Decontamination
- Clinox pickling
- Roughness measurement with certificate
- Quality work at competitive prices
- Strives to comply with all agreed terms and delivery times
- Non-binding offers

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CONTENT

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1. Our references
2. What is stainless steel?
3. Composition and aspect of Rouging
4. Formation of Rouging
5. Effect of Rouging on the stainless steel surface
6. Parameters influencing Rouging formation
7. Derouging of stainless steel surfaces / chemicals
8. pH-neutral Derouging with DIRUNEUTRA
9. Our range of service

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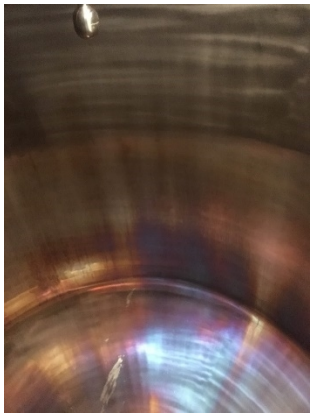
OUR RANGE OF SERVICE

ateco advanced metal finishing

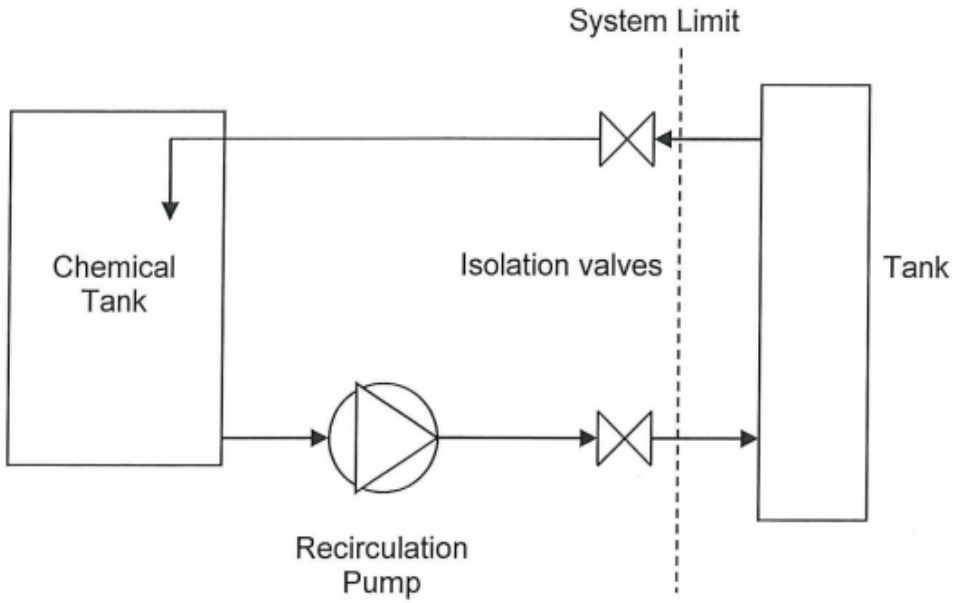
- Cleaning of stainless steel pipe systems and equipment
- Passivation of new stainless steel systems
- Derouging and Passivation of existing systems
- Documentation for all working processes and chemicals
- Treatment of waste water in line with environmental legislation
- Supply with precisely defined chemicals for self-operations



SET UP

4.4.8.1 Recirculation design

Preferred design, if applicable.



CERTIFICATES

ateco

TO WHOM

GMO[1] decl

We – Ateco Service
processing of our p
manipulated organi
during manufacturi

Rheinfelden, April 1
Ateco Tobler AG

Marc Vernier
Managing Director

[1] GMO: Genetically m

TO WHOM IT M

Characteristics of th

- Diruneutra LIQ
- Diruclean NS
- Dirupass NB
- Dirupass AP

This is to confirm that abov
chromates, mercury or hea
Environmental- and toxicity
United States requirements

Rheinfelden, April 1, 2011
Ateco Tobler AG

Marc Vernier
Managing Director

TO WHOM IT MAY CONCERN

TSE / BSE[1] declaration

This is to certify that our products do not contain ingredients of animal origin, nor is there any contact with such materials during manufacturing.

In particular, this statement is applicable and valid for the product

Diruneutra LIQ, Diruneutra P and Diruclean NS

Rheinfelden, April 1, 2014
Ateco Tobler AG

Marc Vernier
Managing Director

[1] The Bovine spongiform encephalopathy (**BSE**) belongs to the group of the transmissible spongiform encephalopathy (**TSE**) diseases

SAFETY SHEETS

	SUBSTRATE COMPATIBILITY	
ateco	DIRUPASS NB	Dok.Nr. 0605-14F

A Passivation solution composed by

2.0 – 10.0% v/v Dirupass NB

can be used on the following materials without hesitation:

a) Plastic:
- PE
- PTFE
- FEP
- PVDF
- EPDM
- Silicone
- PEEK
- Viton®

b) Stainless steel:
- 1.4301
- 1.4401
- 1.4404
- 1.4435
- 1.4571
- 1.4539
- 1.4591

c) Nickel base alloys
- All Hastelloy® types

d) Glass

Other materials on demand and separate clarification.

Confirmed by	Name	Date	Signature
Ateco Tobler AG	Marc Vernier	09.05.2016	

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OUR REFERENCES

ateco advanced metal finishing

- Alcon, FR
- B. Braun, DE
- Biotec Systems, AT
- Boehringer Ingelheim, DE
- Cilag (J&J), CH
- Crucell, CH
- CSL Behring, CH + DE
- EGIS, HU
- Gedeon Richter, HU
- GSK, FR
- Lilly, FR
- ABIGO SE
- Novawax SE
- Akademiskahus SE
- Karolinska Sjukhuset SE
- Recipharm SE
- Cytiva SE
- GE Healthcare SE
- Lohmann & Rauscher, DE
- Lonza, CH
- MCL, NL
- Merck Serono, CH
- Novartis, CH + FR
- Roche Diagnostics, DE
- Roche, CH
- Sankyo Pharma, DE
- Solvay Pharma, NL
- Novo Nordisk, FR
- Pfizer SE
- Astra Zeneca SE
- Octapharma SE
- SOBI SE
- Galderma SE
- Fresenius SE
- Gävle Sjukhus, sterilcentralen
- Perstorp Pharma

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OUR REFERENCES IN USA

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Customer	Contact	Description
Merck West Point, PA	Greg Sanpedro	small parts
Elli Lilly, Indianapolis, IN	Robert Augustine	WFI tank
BI, Bedford, OH	Wendy U	small vessel (flood)
Alcon, Fort Worth, TX	Dough	WFI loop
Sanofi, Swiftwater, PA	Vidal Ruiz	small parts
Bayer Berkely, CA	Joe Garcia	Small parts
Amgen, Boulder, CO	Perry Chavez	small parts
KIK, Toronto, Onterio	Kresimir Kordis	PW loop
WEST Pharma	Dave Maffett	PES3000, WFI loop, WFI tank, and CSG
Talecris	Adam Helsel	Multiple tanks, UF's, and flow cabinets
WEST Pharma	Dave Maffett	WFI tank
Fort Doge Animal Health	Nick Reis	Micselanious parts
Fort Doge Animal Health	Nick Reis	small vessel (flood)
Baxter	Troy Gilstrap	WFI loop and MECO VC
Emergent Bio Solutions	active Chemical	WFI loop and MECO VC
Pfizer Chesterfield, MO	Brady Fischer	WFI tank and loop

ROUGE AFTER DEROUGING

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BEFORE AND AFTER DEROUGING

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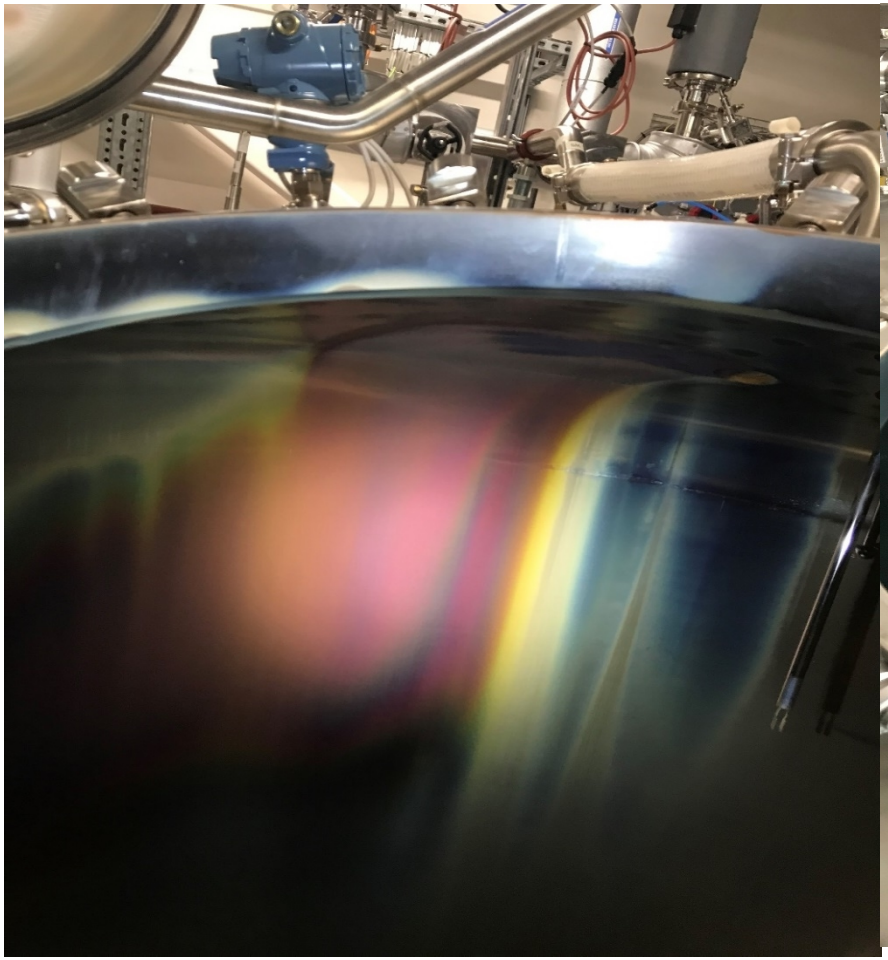


WS MACHINE

WHAT IS STAINLESS STEEL?

Stainless steels are iron based alloys with a chromium content of at least 11%, which represents the minimum amount to prevent atmospheric corrosion.

Stainless steels are designed alloys - mainly based on Fe - containing Cr, Ni, Mo, etc. to improve corrosion resistance by forming a very thin and stabile surface layer – the passive layer.

Classification of stainless steels is based on crystal structure:

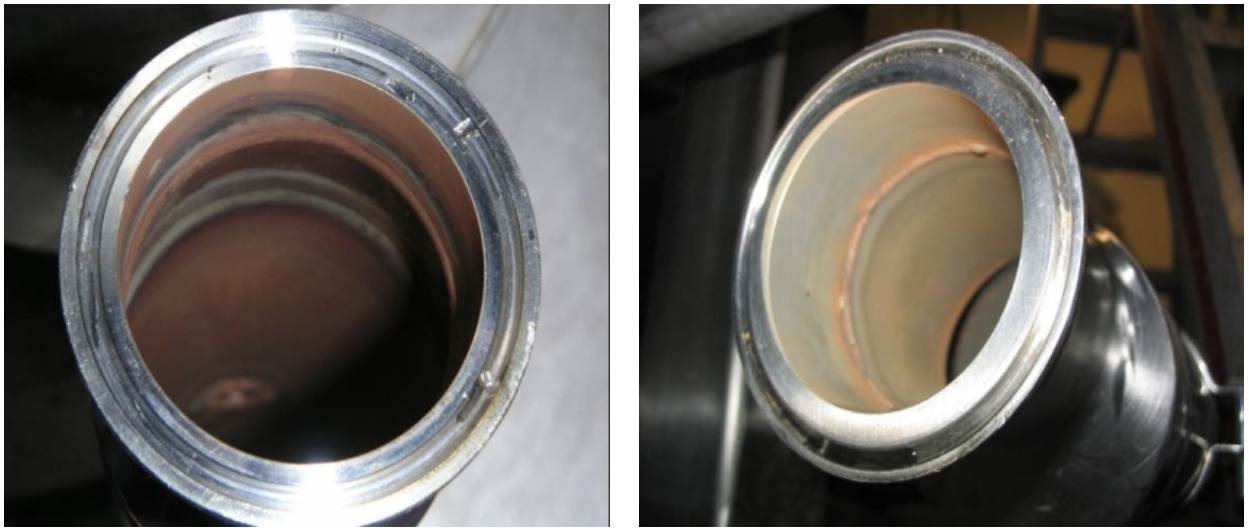
ferritic (body centred cubic unit cell), **austenitic** (face centred cubic unit cell), **austenitic+ferritic** (= Duplex) and **martensitic** (tetragonal body centred unit cell)

WHAT IS ROUGING?
HOW DOES ROUGING LOOK LIKE?

Surfaces of WFI-equipments inspected after 6 – 18 months show often rouging effects:

- Heavy metal-oxide particles preferably Fe-oxides

Example: Rouging in stainless steel pipe

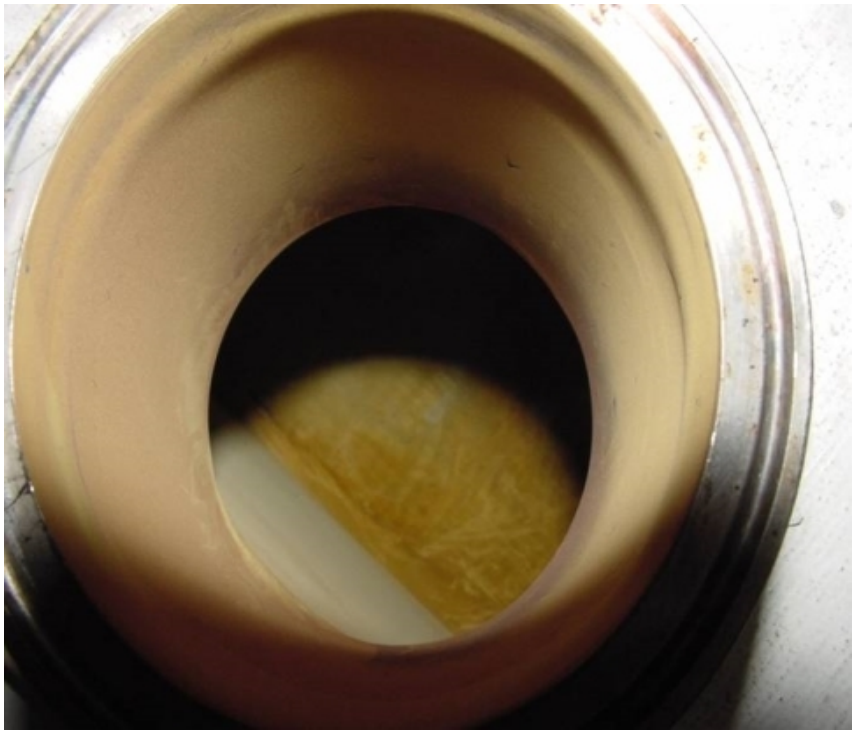


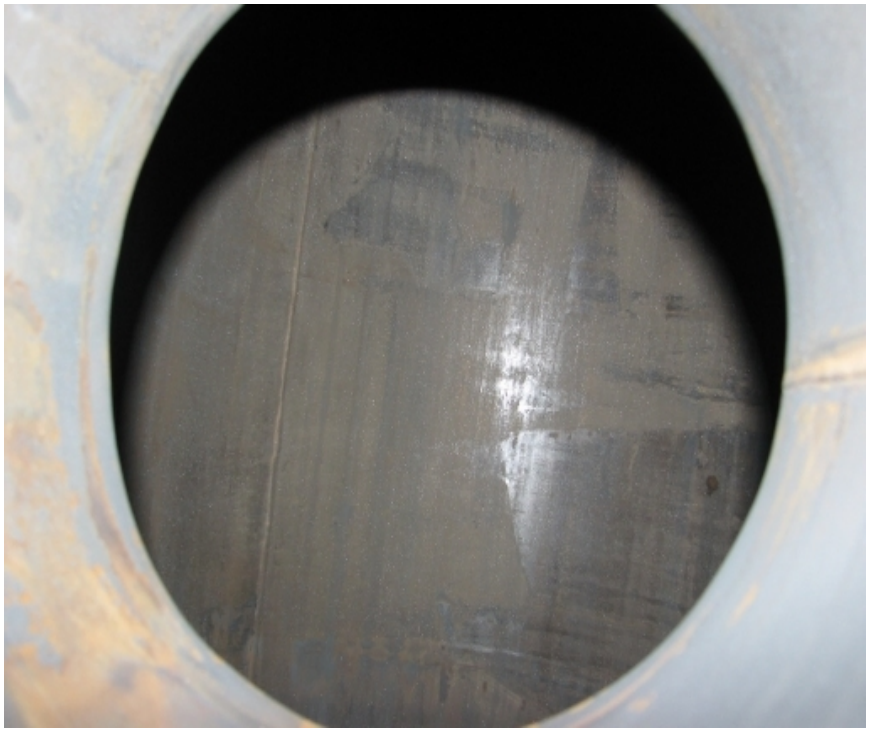
ROUGING IN PRODUCTION FACILITY

- Biotech production
  - Hot WFI (Water for Injection) or AP (Aqua Purificata)
  - Pure steam
  - Production vessels, Purification vessels
  - Fermenters
  - Autoclaves
  - CIP-equipment (Cleaning in Place)

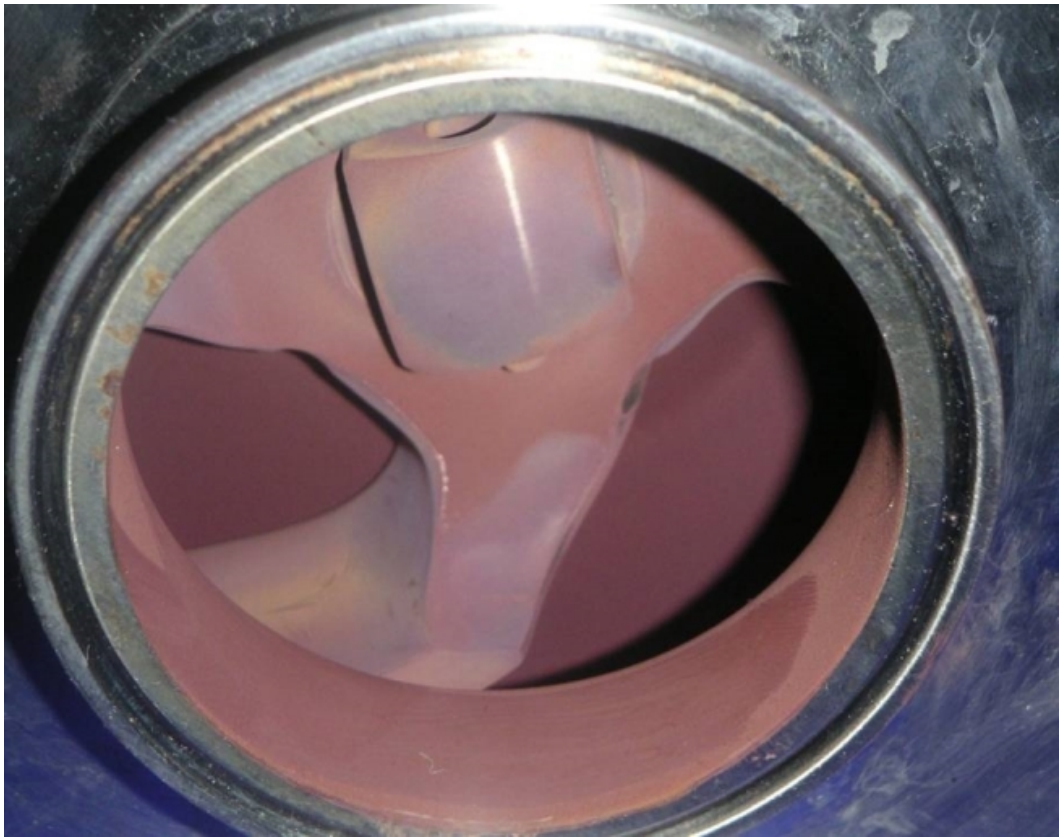
- Chromium Aseptic production
  - Hot WFI (Water for Injection) or AP (Aqua Purificata)
  - Pure steam
  - Production vessels, Storage vessels
  - Freeze driers, Autoclaves
  - CIP-equipment (Cleaning in Place)

ROUGING IN WFI- AND PS-GENERATORS





ROUGING IN WFI-PUMP (CENTRIFUGAL PUMP)



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ROUGING IN WFI-STORAGE TANK

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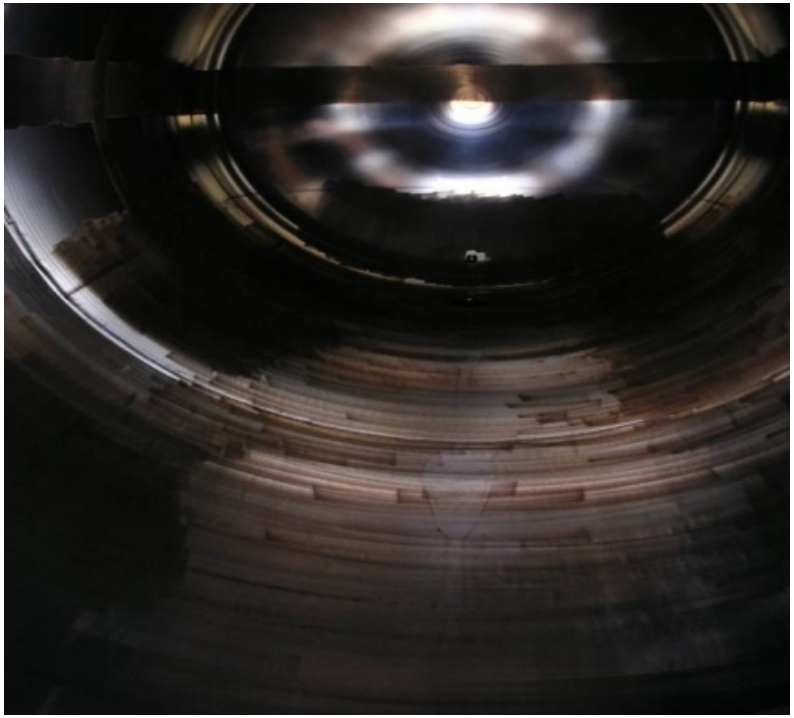

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ROUGING IN PRODUCTION EQUIPMENT

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ROUGING (1)

What is the mechanism of the rouging effect on stainless steel surfaces?

Based on thermodynamically facts, the affinity of Fe to O increases with temperature compared to Cr.

Because of absence respectively low level of O in the hot WFI the repassivation reaction is smaller than the depassivation and the equilibrium is changed remarkably

What happens with the passive layer

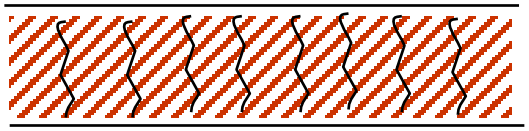
Measurements by Auger and ESCA define the **passive layer** by Cr/Fe-Ratio > 1,5, thickness of layer > 1 … 2,5 nm

1.4404
(ep or mb)

WFI

> 50° C

(thermodynamic effects)



Cr/Fe < 0,5
s = ca. 10 – 1.000 nm
rouge-layer of Fe-oxide at surface (hematite respectively magnetite, uniform corrosion – with increasing micro-roughness)

Source: Dr. Georg Henkel: *Improved corrosion protection,* Chemical Plants and Processing 1/99, S. 50.

INFLUENCED FACTORS (1)

- Grade of stainless-steel (316L, 904L, Al 6XN etc.)
- Surface treatment (mp, ep)
- temperature conditions (< 50° C, 50 – 83° C, > 83° C)
- CO2-content
- O2-content

Reduction of Rouge formation:

- Reduce temperature in WFI systems
- Use correct gas atmosphere in WFI tank systems
- Consider returning cleaning processing operations under controlled conditions for derouging and repassivation

INFLUENCED FACTORS (2)

Which parameters and on which way these parameters influencing rouging?

Based on the results from research of Force-Institute, Denmark, (Pharmaceutical Engineering, July/August 2002) it can be reported:

1.Material grade 1.4435 (316L) mb – **influence of gas atmospheres** at
100° C over 6 weeks:
pure N_2: heavy rouging effects
Air: traces of rouge
80 % N_2, 20 % O_2, no CO_2: very slight respectively no rouging

2.Under N_2 purged conditions material 1.4435 (316L) and 1.4539 (904 L) in mb and ep surface conditions (100° C, 6 weeks):
1.4435 mb: remarkable respectively heavy rouging
1.4435 ep: very low rouging
1.4539 mb: remarkable rouging
1.4539 ep: very slight rouging

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IMPLICATIONS OF ROUGING

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Rouging is principally an inversion of the chromium-oxide enriched, closed passive-layer to an iron-oxide dominated, micro-rough surface.

Rouging is creating heavy metal-oxide particles which can leave the surface uncontrolled to immigrate other system areas.

Following this, we have to take in consideration:

- Particles of heavy metal-oxides
- Increasing micro-roughness of the surface
- Contamination of WFI/clean steam
- No change of conductivity of WFI because Fe is not creating ions

RELEASE OF PARTICLES

The rouge layer consists of heavy-metal-oxides, preferably Fe-Oxides.
The “new” surface layer is not closed and solid –
rouge-particles can be removed.

The rouge-layer consists of particles of heavy-metal-oxides 0,1 … 10 µm which can leave the surface based on stream conditions.

Wipe test of a production vessel

Wipe test of a WFI pipe

ROUGING (1)

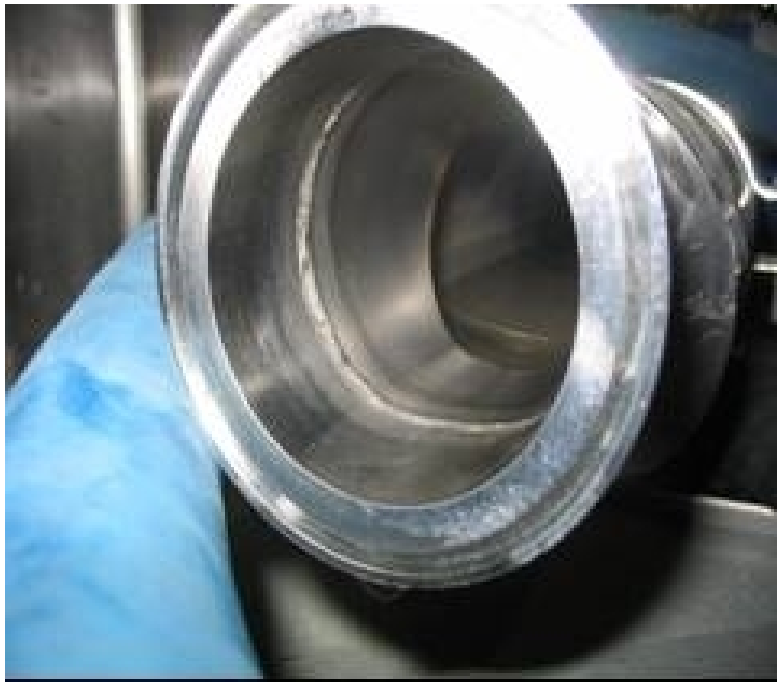
Returning derouging and repassivation operations

- Controlled removal of rouging particles/layer by avoiding surface etching
- Controlled repassivation of stainless steel-surface to reinstall passive conditions
- Controlled removal of all chemical residues used during chemical cleaning/repassivation/rinsing processing
- Using of fully controlled and certified chemicals for derouging/repassivation/rinsing
- Full documentation of the processing (SOP), chemicals, parameters (T, t, concentration) including final measurements and quality checks
- Waste water treatment regarding local government rules

Difficulties of Derouging

- Each system is unique
- Different configuration of Rouging
- Iron oxides are hardly soluble
- With conventional methods no standard Derouging processes possible
- Old systems are more difficult to clean
- Mostly no samples are available
- No time frame → Failure costs of production
- Pure steam systems are hardly to clean

DEROUGING EXECUTION ON SITE



Before - After

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HOW TO REMOVE ROUGING

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- Rouging is composed for the most part of iron oxides/-hydroxides
  - Iron hydroxide, i.e. Iron(III) oxide-hydroxide (Goethite)
  - Iron(II) oxide → Wüstite
  - Iron(III) oxide → Hematite
  - Iron(II/III) oxide → Magnetite
- Rouging can be distinguished into “young” and “old” rouging
- These conditions are a big challenge to find the right and appropriate chemicals to remove the rouging

RISK ASSESSMENT OF DEROUGING CHEMICALS

- Derouging chemical requirements:
  - Dissolving of iron oxides/-hydroxides
  - **No chemical attack on the metal surface**
  - Residue-free rinsable
  - Low chemical concentrations
  - Fast mechanism of action
  - Wide range of efficacy
  - Sprayable
  - Simple waste disposal
  - Low risk in case of a damage

DEROUGING CHEMICALS (1)

- **Strong acid** derouging solutions can contain the following chemicals:
  - Phosphoric acid
  - Sulfuric acid
  - Oxalic acid
  - Citric acid
  - Nitric acid
  - Hydrofluoric acid!!! → Caution: fast surface attack
  - Hydrochloric acid!!! → = good derouging effect → Sustainable destruction of stainless steel
  - Salts containing fluorides (Sodium fluoride, Ammonium bifluoride, etc.)
  - Chelates (EDTA, NTA, etc.)
  - Surfactants

DEROUGING CHEMICALS (2)

- **Soft acid** derouging solutions can contain the following chemicals:
  - Citric acid
  - Oxalic acid
  - Salts (Phosphates, Oxalates, etc.)
  - Chelates (Phosphonates, EDTA, NTA, etc.)
  - Surfactants

- **pH-neutral** derouging solutions can contain the following chemicals:
  - Salts (Phosphates, Oxalates, etc.)
  - Chelates (Phosphonates, EDTA, NTA, etc.)
  - Reducing agents
  - Surfactants

DEROUGING CHEMICALS (3)

Comparison of derouging chemicals

	Strong acid chemicals	Soft acid chemicals	pH-neutral chemicals
Pro	▪ residue-free rinsable ▪ sprayable	▪ residue-free rinsable ▪ sprayable ▪ low acidity ▪ selective for iron oxide/hydroxide ▪ normally no chemical attack on the metal surface ▪ lower costs for waste disposal ▪ lower risk in case of a damage	▪ residue-free rinsable ▪ short derouging time (1 – 4 hours) ▪ selective for iron oxide/hydroxide ▪ wide range of efficacy → standardized processes ▪ low chemical concentration (< 1,5%) ▪ neutral = pH 7 ▪ no chemical attack ▪ low costs for waste disposal → direct to sewerage ▪ no neutralization of rinse water ▪ lower risk in case of a damage
Contra	▪ High acid concentrations (15 – 40%) ▪ mostly high application temperature (> 50°C) ▪ not selective for iron oxide/ hydroxide → dissolves also Cr and Ni from the metal surface ▪ mostly long derouging time (often more than 10 hours) ▪ small range of efficacy → pretests are necessary ▪ high costs for waste disposal ▪ high risk in case of a damage ▪ separate waste disposal of rinse water	▪ high application temperature (> 50°C) ▪ high chemical concentration (> 10%) ▪ long derouging time (often more than 10 hours) ▪ very small range of efficacy → pretests are necessary ▪ neutralization of rinse water	▪ high application temperature (> 50°C) ▪ partially not sprayable

pH-NEUTRAL DEROUGING

Comparison in a laboratory test

Derouging with DIRUNEUTRA

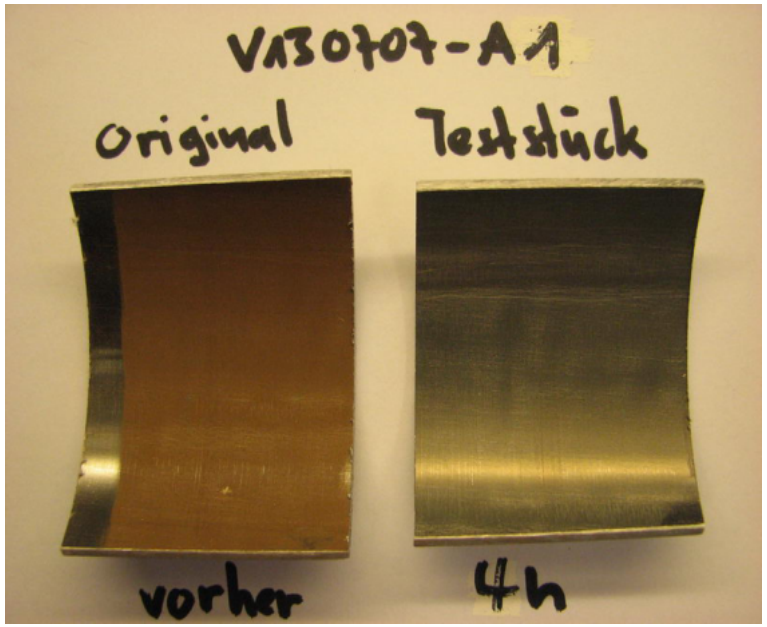
- Sample:
  - A1
- Product: DIRUNEUTRA
- Concentration:
  - 2.5% Diruneutra LIQ/P
- Temperature: 60 - 80°C
- pH: 7
- Time: 4 hours

Derouging with acid

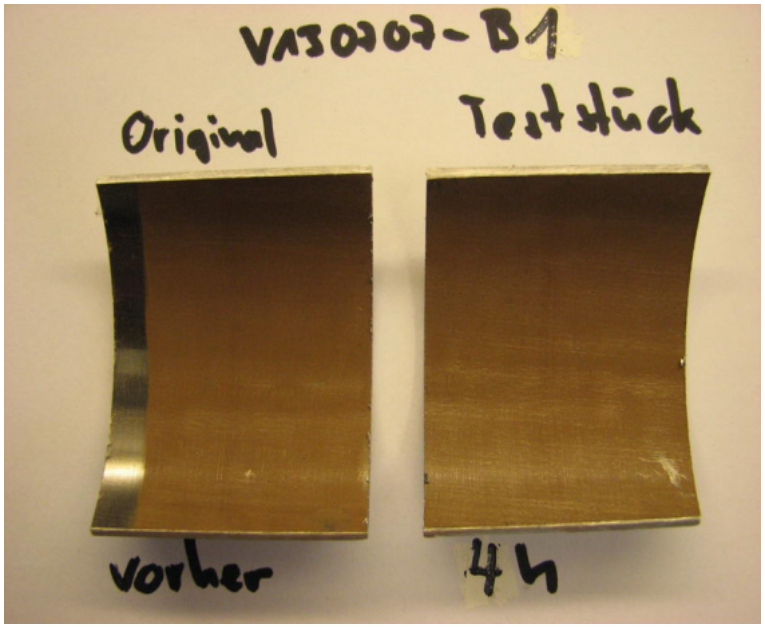
- Sample:
  - B1
- Product: Cleaning agent X with phosphoric acid
- Concentration:
  - 30% X
- Temperature: 70 – 80°C
- pH: < 1
- Time: 4 hours

LABORATORY TEST pH-NEUTRAL DEROUGING

Comparison after 4 hours of treatment



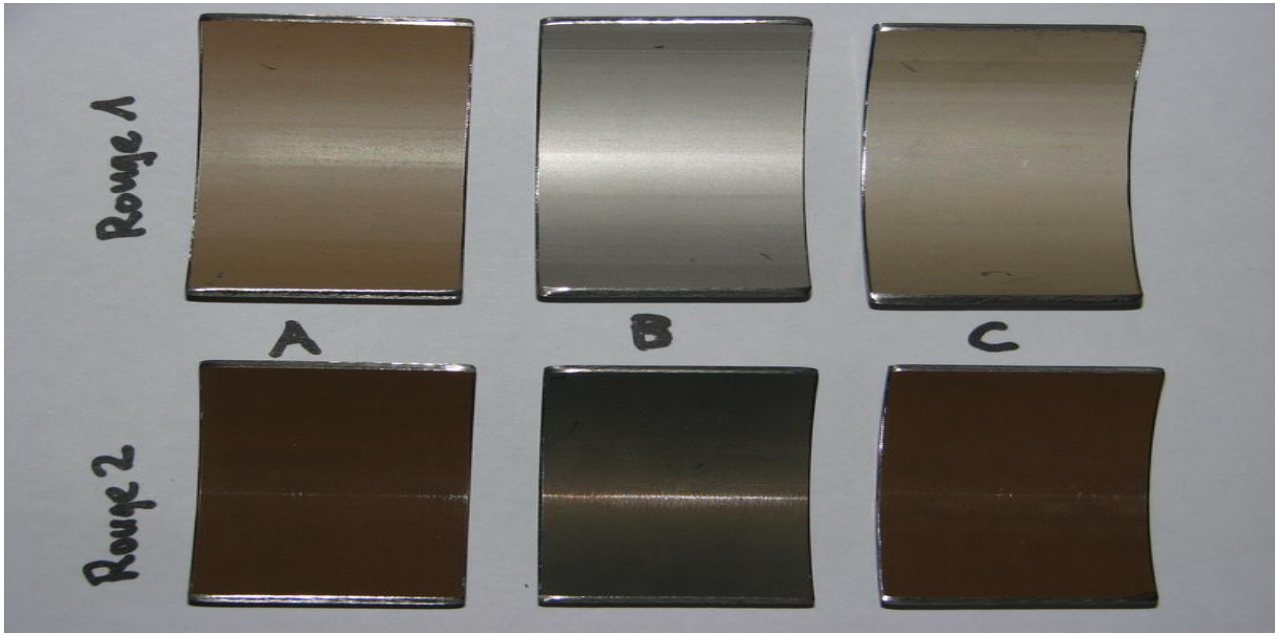
« Diruneutra »



« Product X, acid »

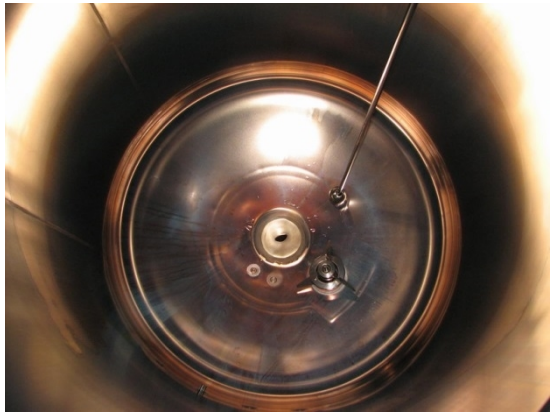
DEROUGING WITH DIRUNEUTRA

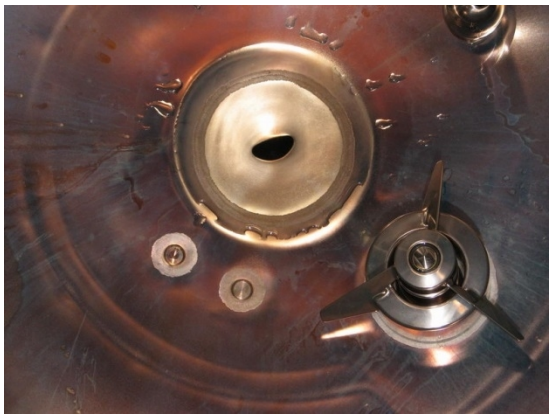
- Rouging 1 and 2 from a hot WFI piping system:
  - Sample A = untreated
  - Sample B = 1,25% Diruneutra, 1 h at 80°C, pH 7
  - Sample C = 15% Phosphoric-/Citric acid solution, 4 h at 80°C, pH < 1



DEROUGING WITH DIRUNEUTRA IN PRODUCTION

before Derouging





after Derouging

CHEMISTRY AND MECHANISM OF ACTION OF DIRUNEUTRA

- Chemical reduction of iron oxide with sodium dithionite

  $Na_2S_2O_4 + 2\ FeOOH \rightarrow 2\ Fe^{2+} + 2\ HSO_3^- + H_2O$

- Chelating agent

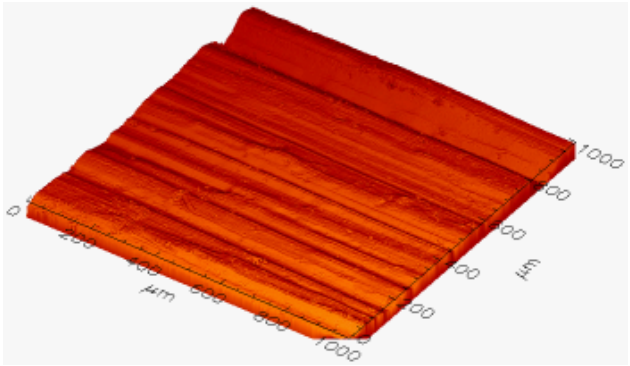
- pH 7

DIRUNEUTRA (1)

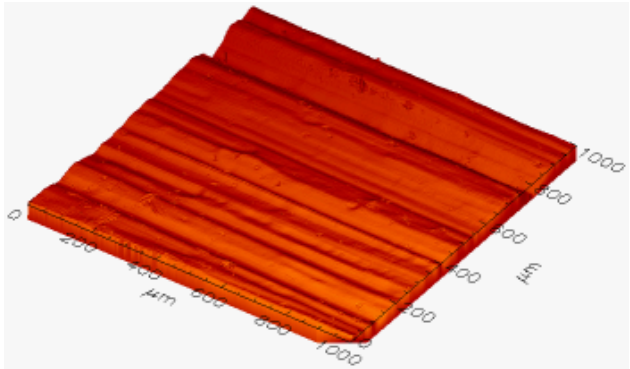
Surface influence of Diruneutra measured with profilometer

-Stainless steel AISI 316L
-Surface electropolished, Ra 0.6 ųm
-Sample dimension: 1.5 cm x 1.5 cm

Before treatment



After 5 treatments with Diruneutra V05

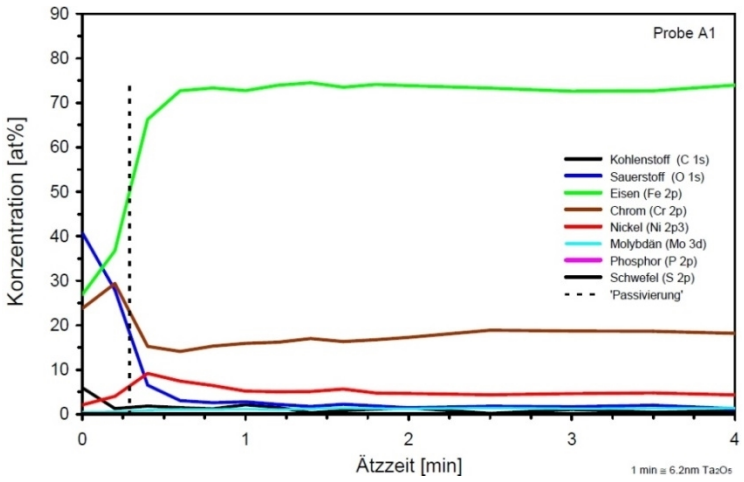


Weight of the sample:	5.33426 grams	5.33417 grams

Surface influence of Diruneutra measured with XPS-analysis

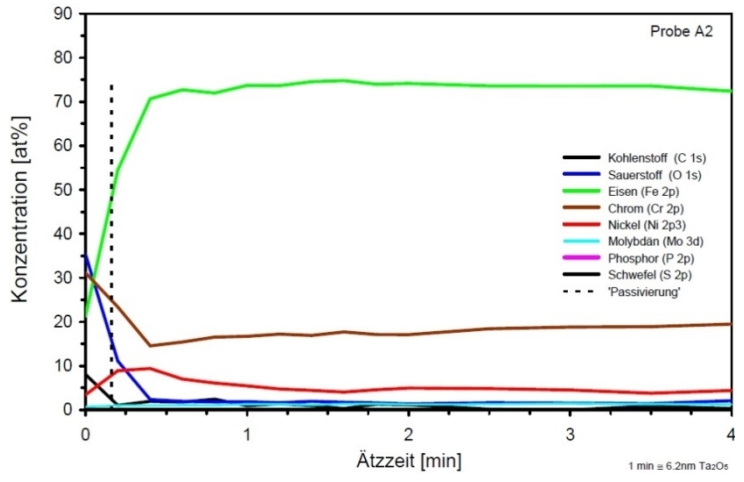
-Stainless steel AISI 316L
-Surface mechanical polished, Ra 0.8 µm
-Sample dimension: 1.0 cm x 2.0 cm

Without chemical treatment



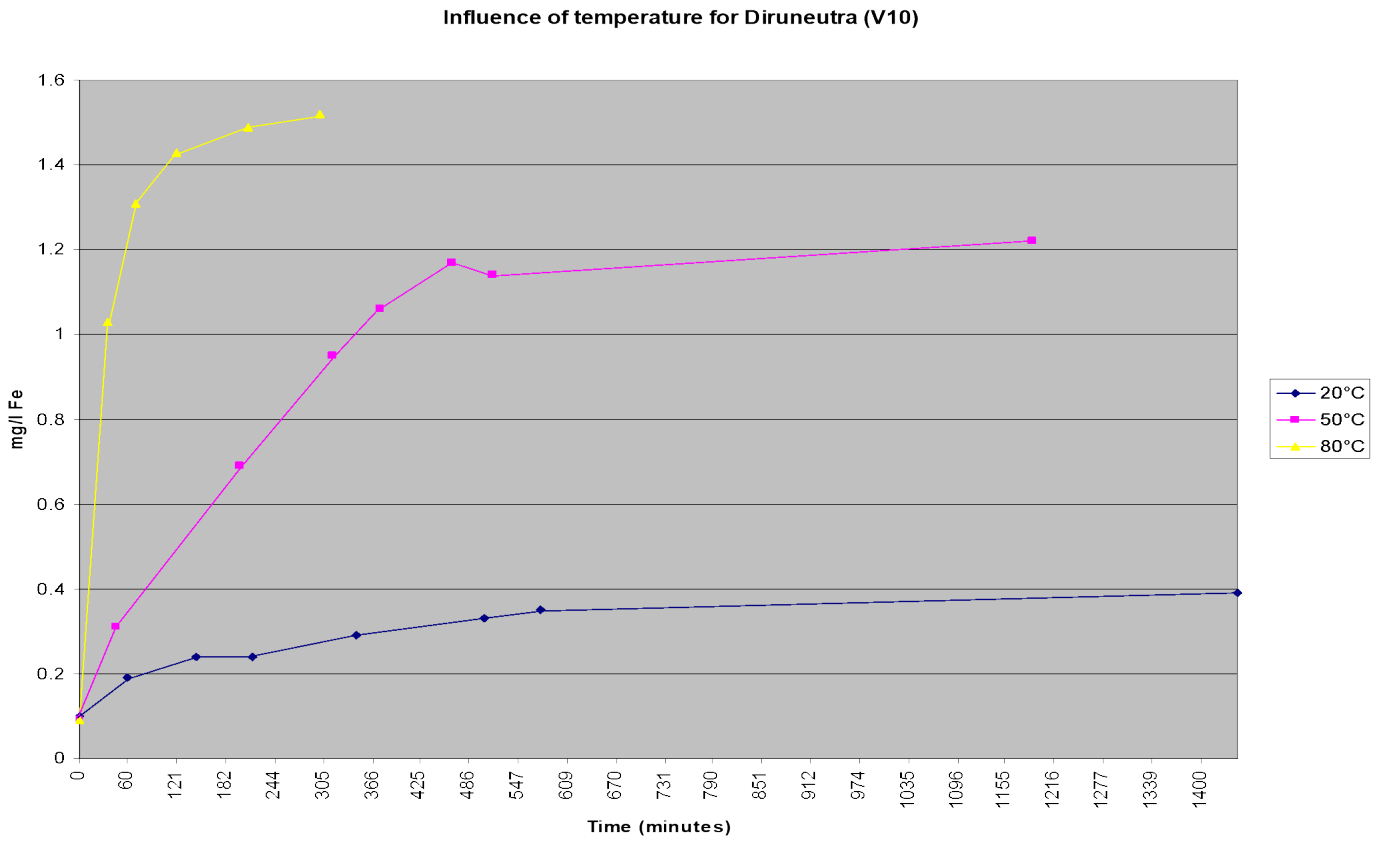
Cr/Fe ratio = 0.5

After 1 treatment with Diruneutra V20 (before passivation)



Cr/Fe ratio = 1.5

Temperature influence for a treatment with DIRUNEUTRA



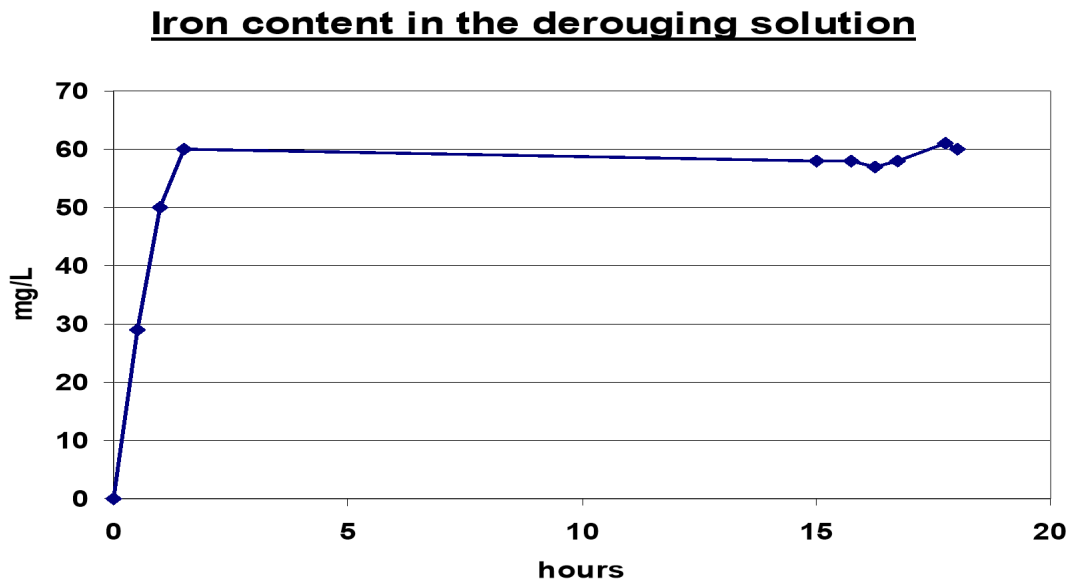
Practical example 1 of a Derouging with DIRUNEUTRA [1]

- Object: WFI Multiple-Effect Distillation unit
  - Columns: 5
  - Capacity: 1100 litres/hour (with 6 bar heating steam)
  - Filling volume: approx. 400 litres
- Derouging and Repassivation procedure
  - Derouging with DIRUNEUTRA V10 at 80°C
  - Repassivation with 3% Dirupass AP at 70°C for 1 hour

- sample picture -

Practical example 1 of a Derouging with DIRUNEUTRA [2]

- Colorimetric iron content measurement (with HACH DR/890)



Practical example 1 of a Derouging with DIRUNEUTRA [3]

- Result:
  - Derouging process was finished after 2 hours process time
  - Iron concentration in the derouging solution: 60 mg/l
  - Amount of removed iron: 30 grams (equal to 43 grams Fe2O3)

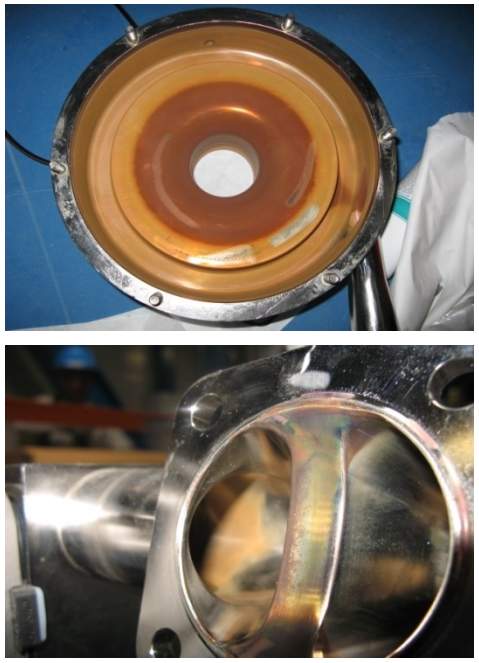
43 grams Fe_2O_3

Practical example 2 of a Derouging with DIRUNEUTRA [1]

- Object: WFI storage tank and 2 distribution loops
  - Storage tank volume: 20’000 Lt
  - Distribution loop volume: 2’000 Lt
  - Total treatment volume: 5’000 Lt

- Derouging and Repassivation procedure
  - Derouging with DIRUNEUTRA V05 at 80°C for 2 hours
  - **Spray process in the vessel by inerting with nitrogen**
  - Repassivation with 2% Dirupass AP at 80°C for 1 hour

Practical example 2 of a Derouging with DIRUNEUTRA [2]

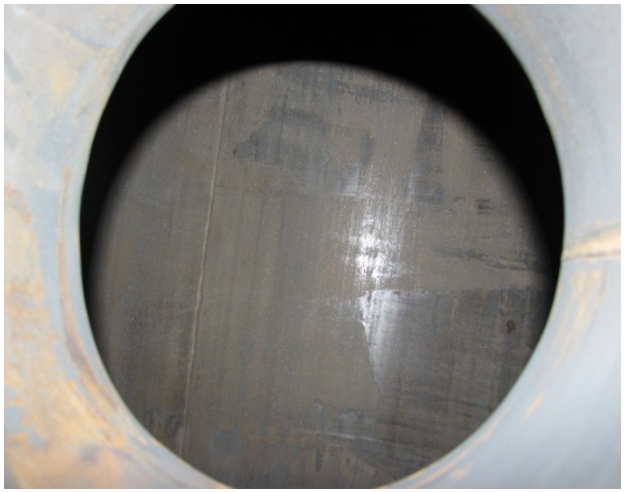


before Derouging

after Derouging

DEROUGING OF CLEAN STEAM SYSTEMS (1)

- Rouging Type 3
- black, partially strong adherent magnetite residues
- black film chemically inert and only removable with strong acids and long process time
- Often incorporates a big amount of red/brown colored rouging particles (Hematite), which can be released from the surface → those particles can be removed by a derouging with DIRUNEUTRA
- Installation work often very time-consuming



Practical example 3: Derouging of a clean steam distribution [1]

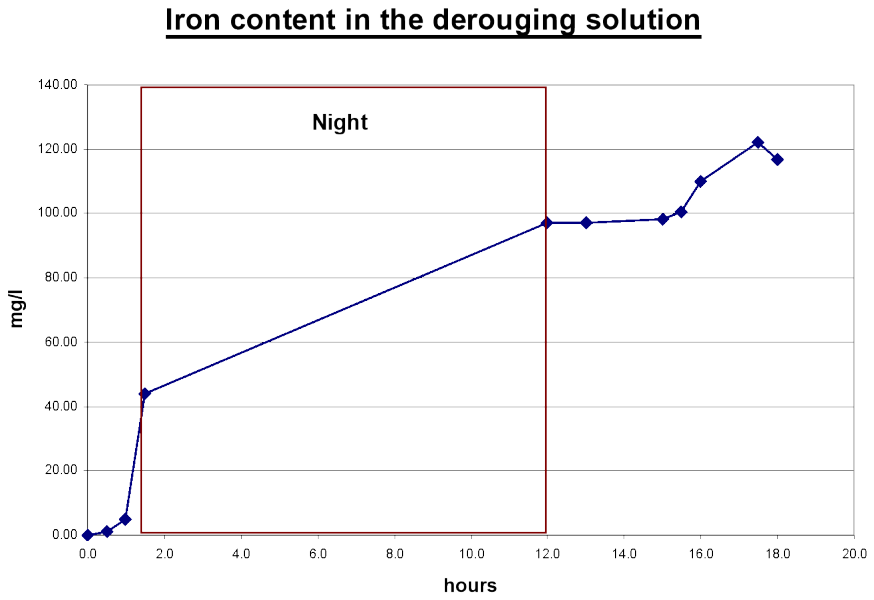
- Object: Clean steam generator with distribution
  - Generator: Typ Stilmas
  - Filling volume generator: 400 Liter
  - Steam distribution: Length 150m, DN25 – 100
  - Filling volume distribution: approx. 300 Lt.

- Derouging and Repassivation procedure
  - Derouging with DIRUNEUTRA V10 at 80°C
  - Repassivation with 2% Dirupass AP at 80°C for 1 hour
  - Total volume: 800 Lt.

- sample picture -

Practical example 3: Derouging of a clean steam distribution [2]

- Colorimetric iron content measurement (with HACH DR/890)



Practical example 3: Derouging of a clean steam distribution [3]

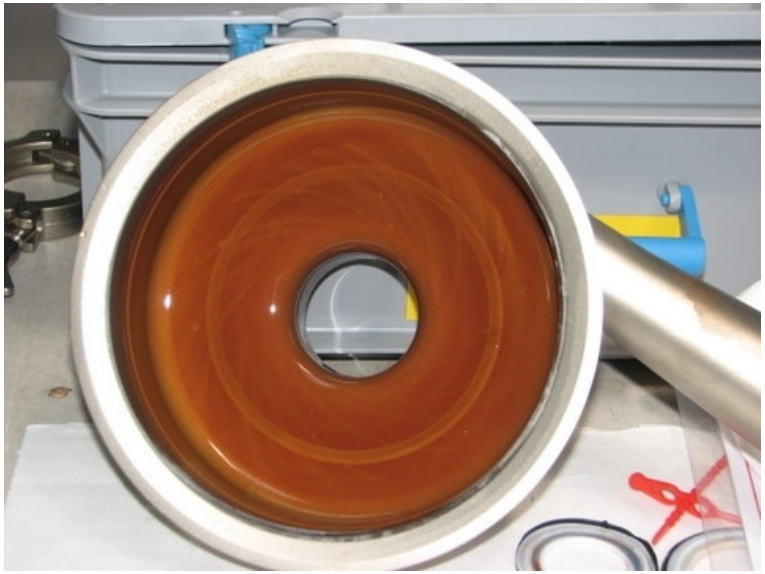
- Result:
  - Derouging solution was left overnight
  - Iron concentration in the derouging solution: 120 mg/l
  - Amount of removed iron : approx. 96 grams (equal to approx. 138 grams Fe_2O_3)

ADVANTAGES OF A NEUTRAL DEROUGING

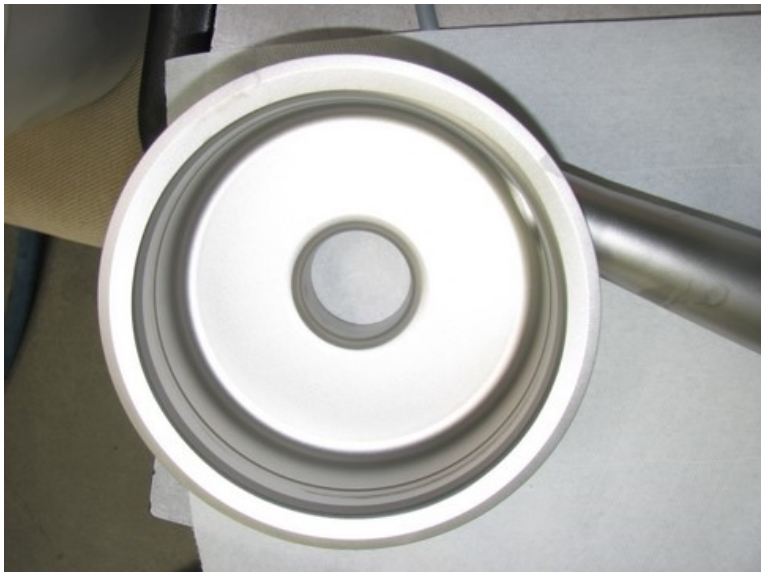
- Shorter process time
- Low chemical concentration
- Wide range of efficacy
- Lower danger for the personnel
- No risk to attack the material surface
- Cost-saving waste disposal of the derouging solution
- Not necessary to neutralize the rinse water
- No damages in case of leakage

Example of derouging with DIRUNEUTRA

Pump cover of a WFI centrifugal pump



before



after

SUMMARY

- We can find Rouging in all pure systems but in different forms, different layer thickness and after different time.
- Mainly Rouging is generated in hot systems.
- Rouging is creating heavy metal-oxide particles which can leave the surface.
- A Derouging operation has to be executed under qualified and controlled conditions.
- This derouging procedures use pH-neutral cleaning solutions instead of acid solutions