Workshop on Pickling Solutions Technology

Surface treatment by pickling with inorganic solutions

13th of November 2019, Düsseldorf

Matthias Kozariszczuk

Dr.-Ing. Matthias Kozariszczuk

BFI Excellence in Applied Research
VDEh-Betriebsforschungsinstitut GmbH
Stahl

Content

VDEh-Betriebsforschungsinstitut GmbH

Introduction

› Motivation of the surface treatment with inorganic acids

Main pickling effects

› Characterisation of the surface treatment

Inorganic acid pickling systems and their related environmental characterisation

› Characteristic for flat steel and coiled wire rod

› Chemical and mechanical pre-treatment

› Inorganic acid systems for the surface treatment and the handling of liquid and gaseous emissions

Outlook – potential improvements and research fields

Introduction

Motivation for the pickling with inorganic acids

- Preparation of a surface quality which allows the further processing of the steel
  - Remove of scale for carbon and stainless steel
  - Remove of e.g. the chromium depleted layer for stainless steel

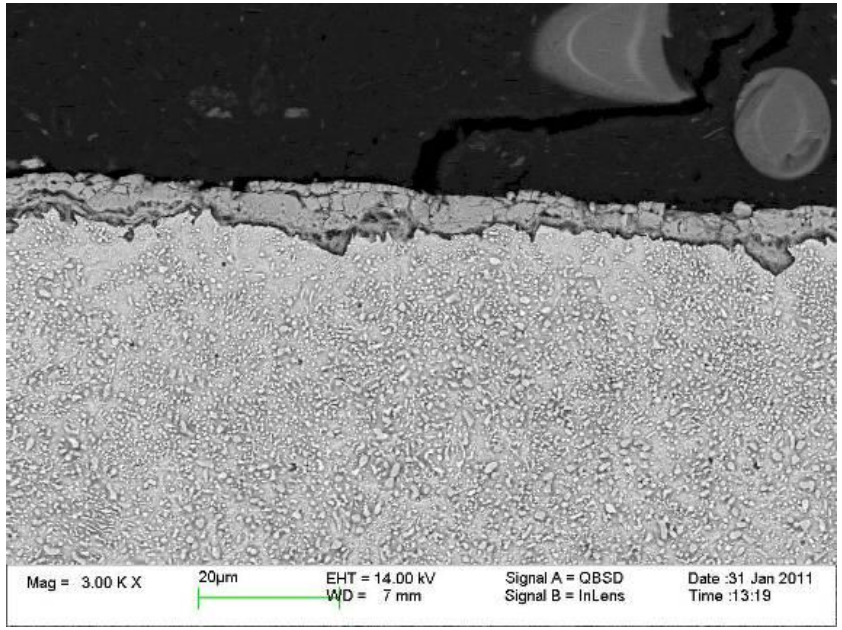
Stainless steel wire rod – before pickling

Stainless steel wire rod – after pickling

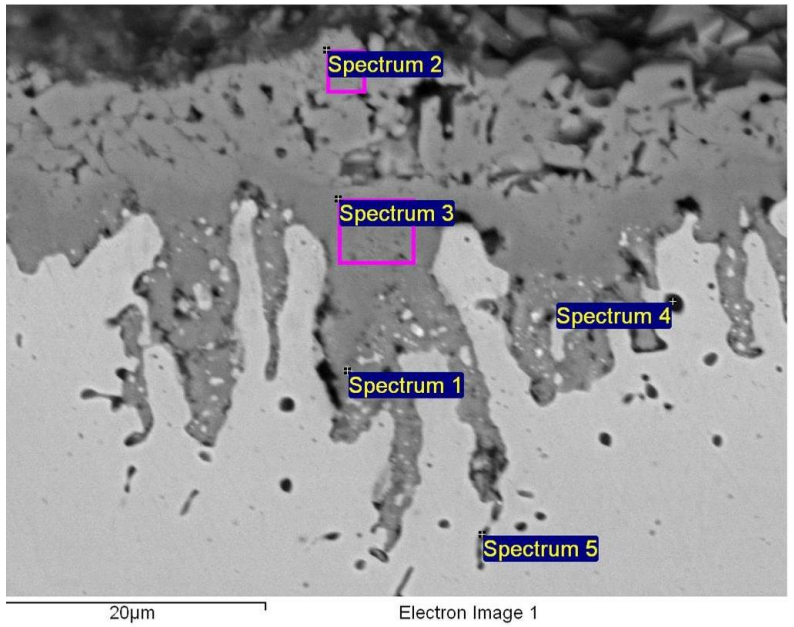
Introduction

Motivation for the pickling with inorganic acids

› Scale removal for the further processing of the steel



SEM picture - 100Cr6 before pickling



SEM picture - 1.4462 before pickling

Introduction

Motivation for the pickling with inorganic acids

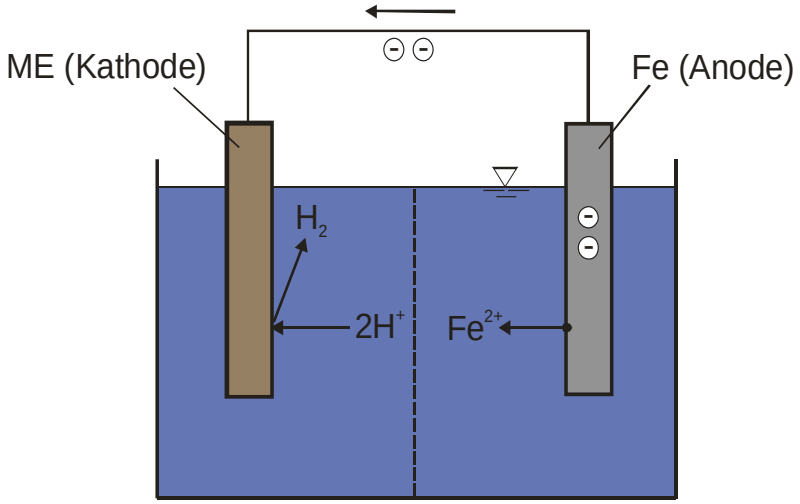
- Production of a surface fitting the request e.g. of the bright steel processes
  - Residual scale on the surface damage the drawing tool and lead to surface defects

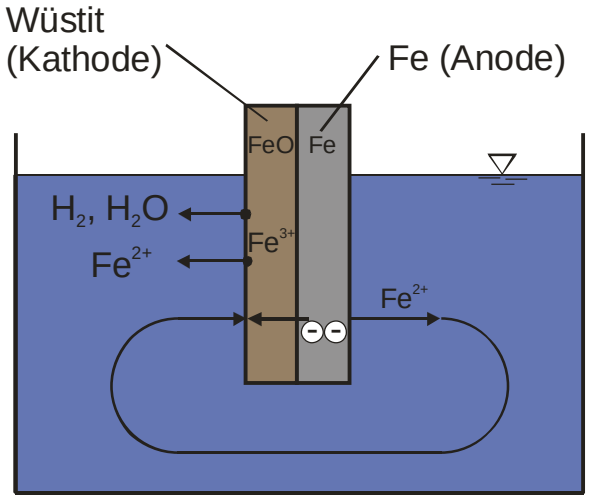
Drawing tool - original
Source: Gerdau

Drawing tool damaged by residual scale (red arrow) – Source: Gerdau

Main pickling effects

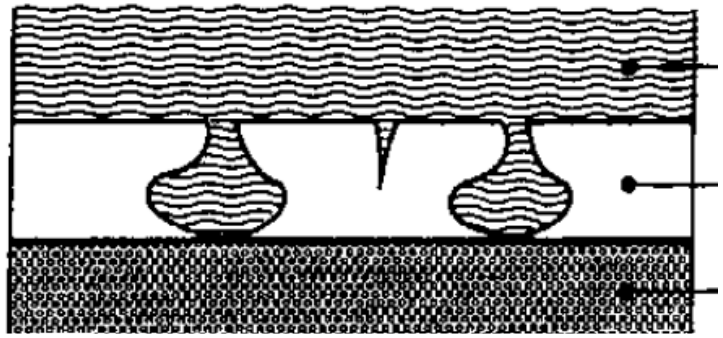
- Electrochemical reaction: formation of a local element of metal surface and metal oxide
- Pickling of steel: Wustite FeO, Magnetite Fe_3O_4, Hematite Fe_2O_3
- Wustite: positive charge („electron lack“) = flexible charge = important electrode for pickling effect (magnetite is similar)
- Hematite: without importance

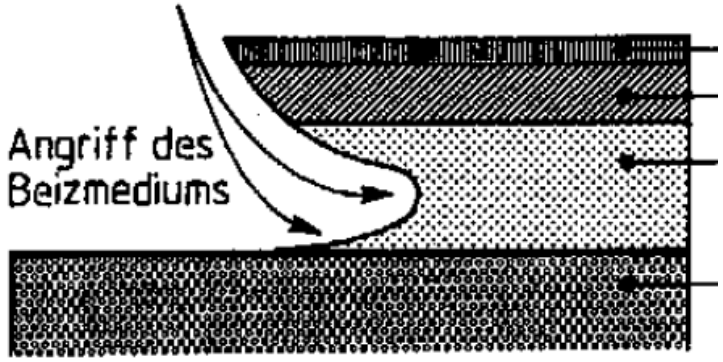


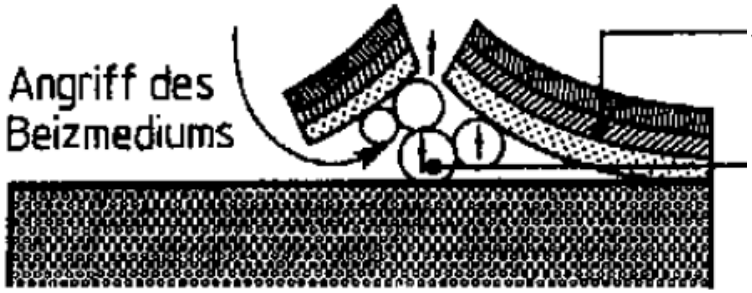


Main pickling effects

3 phases of the pickling process (source: Rituper)







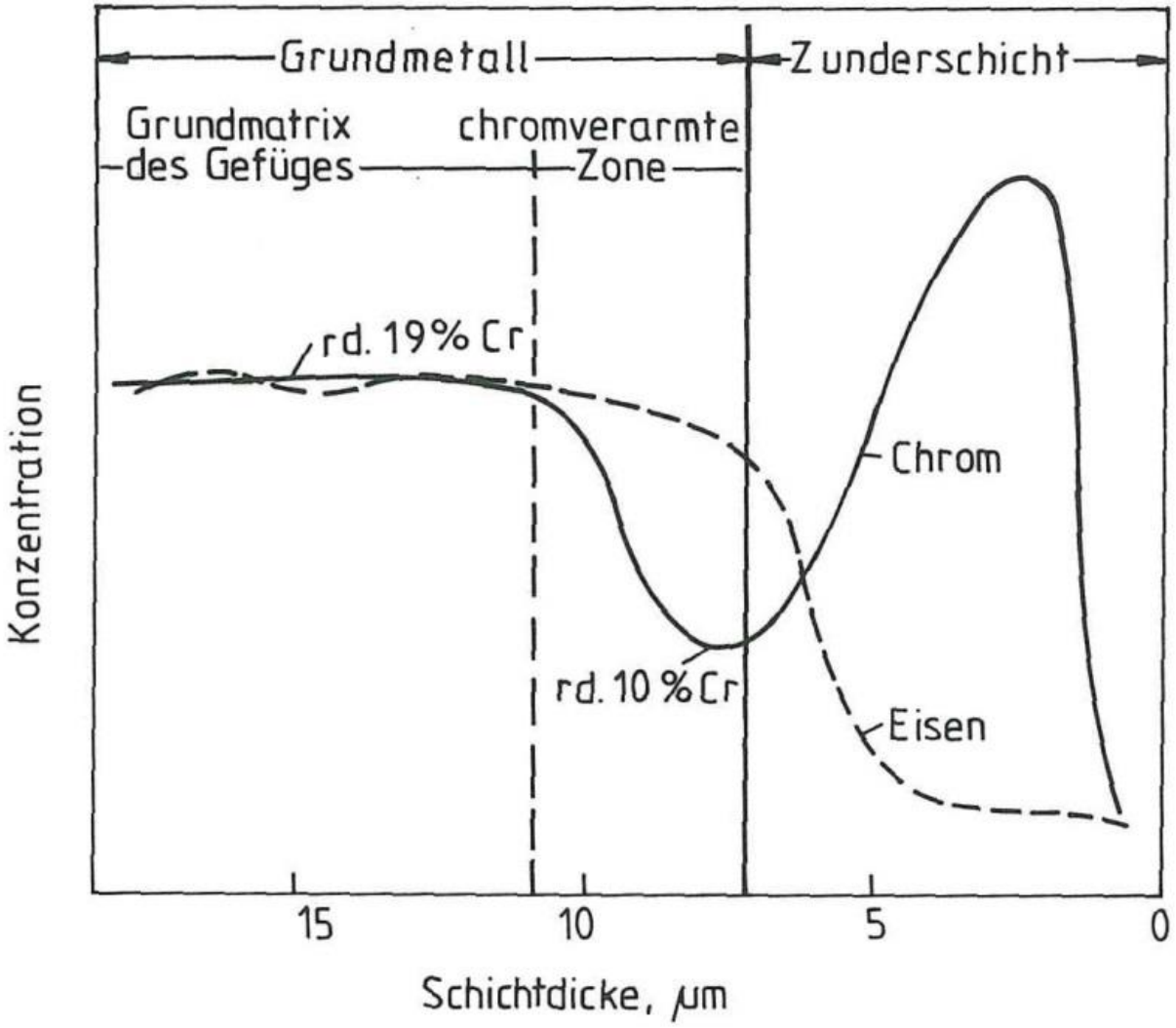
Phase 1 – penetration of the scale by the pickling acid

Phase 2 – removal / solution of scale by the pickling acid

Phase 3 – removal / blasting of residual scale by hydrogen formation

Main pickling effects

Focus to stainless steel - removal of e.g. chromium depleted layer



Scale thickness / chromium depleted layer – stainless steel
Source: Rituper

Inorganic acid systems and the related environmental aspects

VDEh-Betriebsforschungsinstitut GmbH

Pickling of **flat steel or single wire rod**

- Advantages
  - Simple mechanical pre-treatment with shot blasting, brushers, scale-breakers
  - Steel surface is very easy to reach for the pickling acid – very good acid transfer
  - Measurement of the surface quality directly after the pickling process
- Demands
  - Decoiling
  - High coil speed up to 400 m/min - wire speed >10m/min and parallel treatment of 10-40 wire rods for an efficient pickling process – capacity is limited e.g. to 50Tt/a
  - Connection of the processes heat treatment, pre-treatment, pickling, coating

VDEh-Betriebsforschungsinstitut GmbH

Pickling of a **wire rod coil**

- Advantages
  - Processing of the wire rod coil in the format delivered by the rod mitt
  - High production capacity
- Demands
  - Acid penetration of the coil to ensure the mass transfer to the steel surface
  - Alloyed and stainless steel grades demand a chemical or mechanical pre-treatment
  - Changes of the optimal chemical operation point lead to surface defects
  - Surface inspection can be performed offline only

Inorganic acid systems and the related environmental aspects

VDEh-Betriebsforschungsinstitut GmbH

Requirements to the pickling process - surface quality

- Scale free
- Roughness
- Acid free surface
- Metallic surface (stainless steel)

Inorganic acid systems and the related environmental aspects

Chemical and mechanical pre-treatment of **wire rod coils**

› Aim: Improvement of the pickling process

› Main effect: cracking, modification and/or reduction of the scale layer

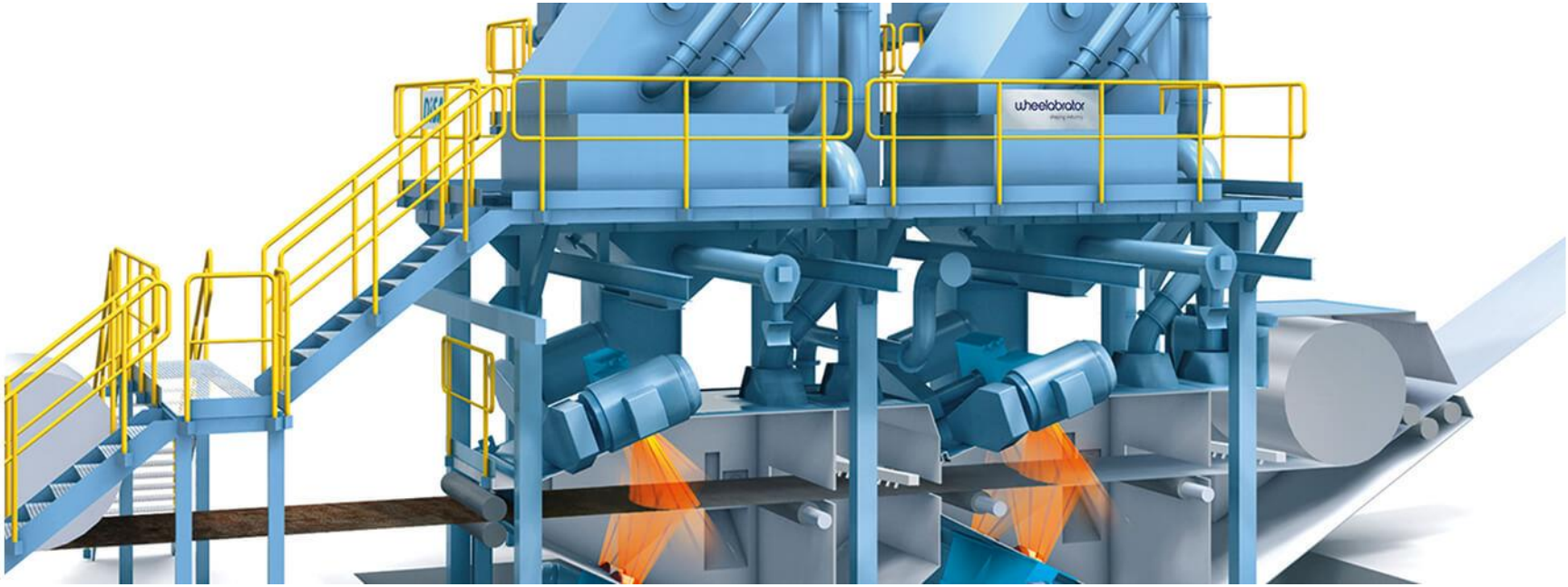
Chemical pre-treatment
Feropur for wire rod coils – source Bochemie

Mechanical pre-treatment
Shoot blaster for wire rod coils – source Fa. CYM

Inorganic acid systems and the related environmental aspects

Mechanical and chemical (stainless steel) pre-treatment of **flat steel and single wire rod**

› Processor, shot blaster, grinding brushes, pre-pickling (electrolytic) for stainless steel

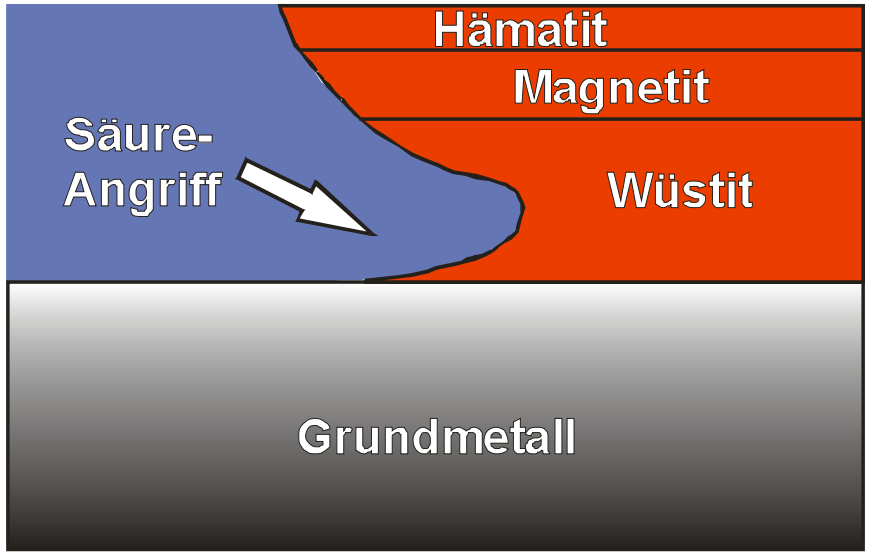


Mechanical pre-treatment
Shoot blaster for flat steel – source wheelabrator

Inorganic acid systems and the related environmental aspects

Reminder: phases of pickling process

- Penetration of the scale layer with acid
- Reaction of acid and metal oxide with formation of metal salts
- Reaction of acid with the steel with formation of hydrogen and metal salts



Typical inorganic pickling acids

- Hydrochloric acid HCl – costs (incl. supply and disposal): 37 €/m³$_{\text{operational acid*}}$
- Sulphuric acid H2SO4 - costs: 16 €/m³$_{\text{operational acid*}}$
- Mixed acid – nitric and hydrofluoric acid - costs: 60-70 €/m³$_{\text{operational acid*}}$

**Value is related to average operational concentration*

Inorganic acid systems and the related environmental aspects

VDEh-Betriebsforschungsinstitut GmbH

Pickling with hydrochloric acid

- Characterisation
  - Strong acid
  - Me + 2 HCl > $MeCl_2$ + H_2
  - Oxide solubility Rituper
    - Fe_2O_3, Fe_3O_4, Cr_2O_3, CrO_3, MoO_3, Mn_3O_4, NiO, SiO_2, V_2O_3, V_2O_5
- Application
  - Typical for carbon steel
  - Treatment of stainless steel only in combination with hydrofluoric acid or oxidants – demand: scale breaking
- Advantages: price, implementation range, simple infrastructure
- Disadvantages: limited oxide solubility, selective corrosion, over-pickling

Inorganic acid systems and the related environmental aspects

Hydrochloric acid – handling of emissions and environmental impact

- Emissions: chlorine gas, rinsing water, spent acid
- Cycle management – technical / economical feasible
  - Total regeneration of the spent acid – pyrohydrolysis
  - Concentration of rinsing water is possible but up to now not relevant
- Acid- and rinsing water treatment: neutralisation, precipitation, sludge separation – limit values for chloride up to no not critical
- Special applications to increase the pickling efficiency
  - HCl – HF: effect – formation of metal complexes, improved solubility of metal oxides
  - HCl – oxidants: effect – improved pickling efficiency by conversion of Fe(II) to Fe(III)

Inorganic acid systems and the related environmental aspects

VDEh-Betriebsforschungsinstitut GmbH

Pickling with sulphuric acid (H_2SO_4)

- Characterisation
  - High metal capacity
  - Me + 4 H_2SO_4 > $Me(SO_4)_2$ + $Me(SO_4)$ + H_2O
  - Oxide solubility Rituper
    - Fe_2O_3, Fe_3O_4, Cr_2O_3, CrO_3, MoO_3, Mn_3O_4, NiO, SiO_2, V_2O_3, V_2O_5
- Application
  - Typical for carbon steel, treatment of stainless steel as pre-pickling process or in combination with hydrofluoric acid or oxidants (Cleanox)
- Advantages: price, low amount of gaseous emissions, high pickling efficiency especially between 85°C und 95°C
- Disadvantages: limited oxide solubility, potential overpickling

Inorganic acid systems and the related environmental aspects

VDEh-Betriebsforschungsinstitut GmbH

Sulphuric acid – handling of emissions and environmental impact

- Emissions: sulphate containing vapor, rinsing water, spent acid
- Cycle management – technical / economical feasible
  - Total regeneration of the spent acid by crystallisation – recycling of free acid by retardation
  - Concentration of rinsing water with lower concentration than 1500mgsulphate/L with ion exchanger or membrane filtration
- Acid-and rinsing water treatment: neutralisation, precipitation, sludge separation – limit values usually <1000mg/L
- Special applications to increase the pickling efficiency for stainless steel
  - H_2O_2 – HF + Additives (Cleanox): effect – improvement of the surface quality – not for all steel grades feasible (e.g. duplex-steels)

Inorganic acid systems and the related environmental aspects

Pickling of stainless steel with mixed acid containing nitric- and hydrofluoric acid (HNO_3 + HF)

- Characterisation
  - High metal capacity, high pickling efficiency
  - $Me + HNO_3 > Me^+ + NO_x + H_2O$
  - $Me^+ + HF > MeF + H^+$
  - Oxide solubility Rituper
    - Fe_2O_3, Fe_3O_4, Cr_2O_3, CrO_3, MoO_3, Mn_3O_4, NiO, SiO_2, V_2O_3, V_2O_5
- Application
  - Only for stainless steel
- Advantages: best surface quality, high pickling efficiency
- Disadvantages : formation of NO_x, high price, effort for emission treatment

Inorganic acid systems and the related environmental aspects

Nitric and hydrofluoric acid – handling of emissions and environmental impact

- Emissions: NOx, rinsing water, spent acid
- Cycle management
  - Recycling of the spent acid with the pyrohydrolysis process – recycling of free acid by retardation
  - Treatment / concentration of rinsing water can be performed with ion exchanger or membrane filtration
- Acid-and rinsing water treatment: neutralisation, precipitation, sludge separation – limit values depending on the local regulation

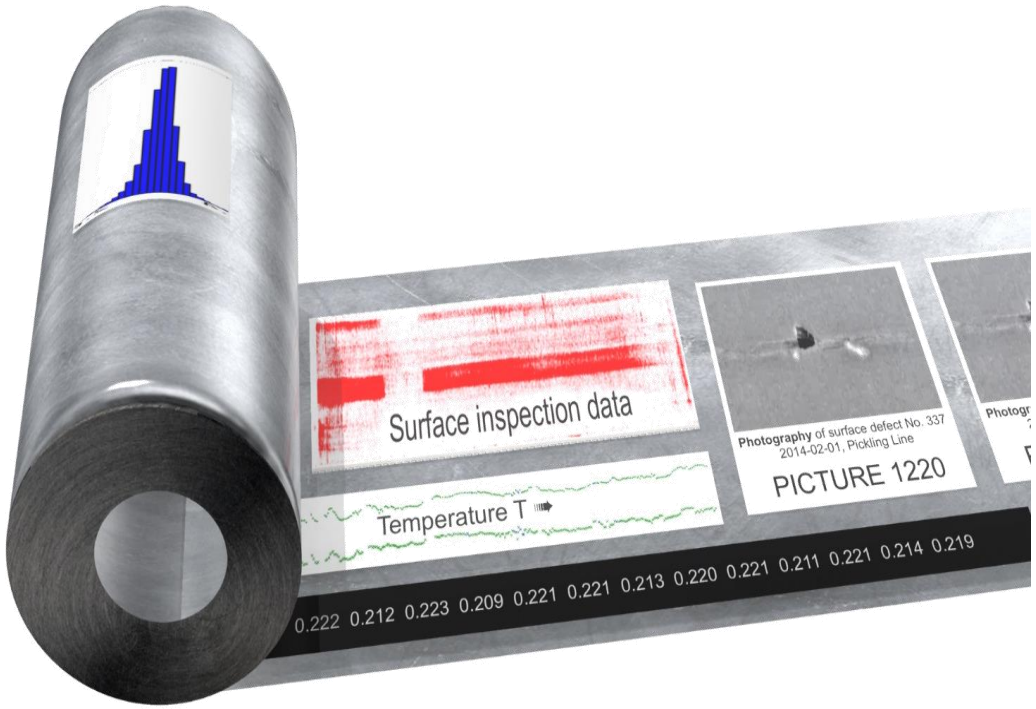
Potential improvements

Coil as a digital twin for improved pickling

Aim: optimization of the coil temperature at the entrance of a HCl pickling line

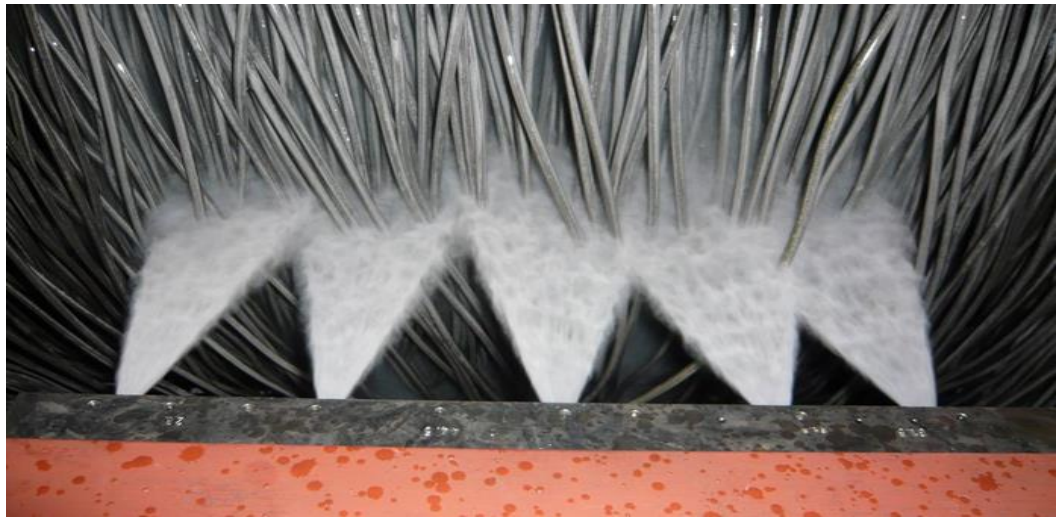
Use models

- Logistical model
- Forecast model for scale
- Pickling model
- Temperature model



Potential improvements pickling of wire rod coils

- Mechanical descaling between pickling steps
  - Application of a high pressure descaler between different pickling steps
  - Removal of swabable scale and contact marks



High pressure descaler – Pilot trials – source: BFI, stahl&eisen

Research fields

- Application / development of online analytic
- Coil as a digital twin
- Forecast of the pickling bath activity to define the optimal pickling program
- Recovery / valorisation of valuable compounds from acids and rinsing water
- Alternative recycling process for HCl with lower CO2 impact

Contact: Matthias Kozariszczuk
VDEh-Betriebsforschungsinstitut GmbH
Stahl-Zentrum · Sohnstraße 65 · 40237 Düsseldorf
Telefon +49 211 6707-494 · Fax +49 211 6707-923 494
E-Mail Matthias.Kozariszczuk@bfi.de· www.bfi.de