Surface treatment by pickling with inorganic solutions

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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

*Source: Gerdau*
Main pickling effects

› Electrochemical reaction: formation of a local element of metal surface and metal oxide

› Pickling of steel: Wustite FeO, Magnetite Fe₃O₄, Hematite Fe₂O₃

› 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

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
Inorganic acid systems and the related environmental aspects

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

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
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 €/m$^3$ operational acid*
› Sulphuric acid H2SO4 - costs: 16 €/m$^3$ operational acid*
› Mixed acid – nitric and hydrofluoric acid - costs: 60-70 €/m$^3$ operational acid*

*Value is related to average operational concentration
Inorganic acid systems and the related environmental aspects

Pickling with hydrochloric acid

› Characterisation
  › Strong acid
  › $\text{Me} + 2 \text{HCl} \rightarrow \text{MeCl}_2 + \text{H}_2$
  › Oxide solubility (Rituper)
    › $\text{Fe}_2\text{O}_3, \text{Fe}_3\text{O}_4, \text{Cr}_2\text{O}_3, \text{CrO}_3, \text{MoO}_3, \text{Mn}_3\text{O}_4, \text{NiO}, \text{SiO}_2, \text{V}_2\text{O}_3, \text{V}_2\text{O}_5$

› 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

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

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 1500mg sulphate/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)
Pickling of stainless steel with mixed acid containing nitric- and hydrofluoric acid (HNO$_3$ + HF)

› Characterisation
  › High metal capacity, high pickling efficiency
  › Me + HNO$_3$ \rightarrow Me$^+$ + NO$_x$ + H$_2$O
  › Me$^+$ + HF \rightarrow MeF + H$^+$
  › Oxide solubility Rituper
    › Fe$_2$O$_3$, Fe$_3$O$_4$, Cr$_2$O$_3$, CrO$_3$, MoO$_3$, Mn$_3$O$_4$, NiO, SiO$_2$, V$_2$O$_3$, V$_2$O$_5$

› 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
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