ТЕХНОЛОГИИ ОБРАБОТКИ МАТЕРИАЛОВ

SUSTAINABLE STAINLESS STEEL – A REVIEW
ON ACID REGENERATION SYSTEMS FOR APPLICATION
IN CONTINUOUS PICKLING LINES

Rögener F.[1], Lednova Yu.A.[2], Andrianova M.Yu.[2], Lednov A.V.[3]

[1]Institute of Chemical Process Engineering and Plant Design, TH Köln, Germany
[2]Peter the Great St.Petersburg Polytechnic University, St. Petersburg, Russia
[3]Nosov Magnitogorsk State Technical University, Magnitogorsk, Russia

Abstract. Steels go through several processing steps to reach the desired state of delivery. Properties and quality of stainless steel are mainly determined by the quality of the product surface. In high temperature processes, such as annealing, rolling and forging, scale layers of 5 to 10 µm thickness consisting of oxides and oxide hydrates are formed on the steel surface. Furthermore, underneath the scale layer the chromium content of the alloy is depleted by diffusion effects, leading to reduced chemical stability. Thus, the chemical removal of both the scale layer and the chromium depleted layer in pickling processes is a fundamental step to achieve clean and homogeneous surfaces. Most of the steels are pickled at least once, usually several times. Strong mineral acids are commonly applied as pickling media. For stainless steel pickling, usually mixtures of nitric acid and hydrofluoric acid – so called mixed acids - are applied. Due to the chemical reaction, an enrichment of the pickling medium with detached scale particles, dissolved metal salts (bound acid), as well as a depletion of active acid (free acid) takes place. In this way, the pickling medium loses its effectiveness and must be replaced or refreshed. This causes significant emissions of acidic waste streams, which need to be treated to comply with regulations. The waste streams contain considerable amounts of dissolved heavy metals, nitrates, and free acid. Commonly, precipitation neutralization is applied; however, this leads to a loss of the dissolved valuables. Furthermore, significant amounts of neutralization sludge are generated, which need to be disposed of, as they constitute hazardous wastes. For both environmental and economic reasons the loss of valuables should be avoided. For this reason, pickling media are continuously regenerated in modern pickling lines. The focus may be on acid recovery only - this is referred to as partial regeneration - or on a combined acid and metal recovery - this is referred to as total regeneration.

Keywords: Stainless steel finishing, pickling, acid pickling, scale removal, acid recovery, metal recovery.

Introduction

Stainless steels are designed especially for demanding, high-quality applications, where heat resistance, chemical resistance or resistance against any kind of corrosion is required. The term "stainless steel" comprises a group of alloys mainly based on iron, carbon and chromium. Chromium serves for the formation of a dense, tightly adherent passive layer, which separates the alloy from the medium [1]. The passive layer consists of different and hard chromium oxides, as well as a chromium depleted metal layer of several µm thickness underneath the oxide layer. Chromium depletion leads to reduced corrosion resistance [2].

To improve specific properties – such as hardness, strength or corrosion resistance – further alloy-

ing elements are added, such as nickel, manganese or others [3, 4].

Worldwide, there is a growing demand for stainless steel products in food and beverage [5], chemical, nuclear [6, 7], oil and gas industries [8]. It has become increasingly popular to prevent reinforcement corrosion of buildings, transport and energy infrastructures [9, 10]. Stainless steel is used as bipolar plate material for the production of Proton exchange membrane fuel cells (PEMFC) [11–13].

The ever-increasing globalization of the world economy has led to a shift in the market shares of stainless steel producing countries. In 2017, more than 50% of all stainless steel melt shop products were generated China, s. **Table 1**.

Increasing stainless steel production exacerbate global environmental problems, if the production does not follow the best available technologies. Cold rolling lines – comprising a combination of different annealing and pickling steps – generate

Table 1

Stainless melt shop products in 1,000 metric tons
in 2008–2017 [14]

Country/Region	2011	2012	2013	2014	2015	2016	2017
China	14,091	16,087	18,984	21,692	21,562	24,938	25,774
Total EU	7,559	7,455	7,147	7,252	7,169	7,280	7,377
Germany	1,502	1,313	1,091	864	459	414	436
Russian Federation	125	112	152	123	95	90	n.i.
USA	2,074	1,977	2,030	2,389	2,346	2,481	2,754
Total World	33,621	35,917	38,130	41,686	41,548	45,778	48,081

n.i. not indicated

gaseous, solid and liquid waste products that are hazardous and toxic for the environment. Prevention, reuse and recycling can be achieved by implementing a number of BATs that are briefly introduced in the following.

Only when the stainless steel surface is clean and homogeneous, a passive oxide film based on oxides and hydroxides of chromium can be formed that is chemically inert [1, 15].

Hot working of stainless steel – such as annealing, rolling and forging - is always accompanied by oxidation and chromium diffusion phenomena, thus surface finishing is an essential production step, which may comprise mechanical treatment, electrolytic descaling, and chemical pickling followed by water rinsing [16, 17].

Microstructure of the steel and complexity of scale layers influence the mechanism and kinetics of pickling. The respective microstructure of the respective steel grade – austenite, ferrite, martensite, and duplex steel – require different heat treatment (annealing) conditions – such as varying temperatures and annealing times, as well as reducing and oxidizing furnace atmospheres. This leads to the formation of complex multilayered oxides. Scale formed during annealing of standard austenitic steels AISI 301, 304L and 309L is dense and has a thickness < 1 µm, whereas the scale formed during hot rolling and annealing was found to have a thickness > 1 µm and a more porous structure [18].

Only a clean, homogeneous stainless steel surface has a high corrosion resistance [19]. Accordingly, scale and chromium depleted layer need to be removed from the surface. Also, the generation of surface defects caused by hot and cold rolling have a significant effect on the pickling process [18].

Scale layers are complex in structure. Therefore, the descaling process for stainless steels comprises several steps, such as mechanical descaling, electrolytic pickling and final chemical pickling, occasionally a subsequent blank pickling and passivation of the surface takes place. For pickling of high-alloyed austenitic grades, higher acid concentrations are required than for ferritic grades. There is no pickling solution, which can be applied for all kinds of stainless steels. On the one hand, this depends on the fact that the respective oxides and base metals have a very different dissolution behavior. On the other hand, the different dissolved metal ions show different inhibiting influence on the dissolution of the base metal. Therefore, optimal acidity and optimum metal concentration must be found for each material group [20]. Pickling of stainless steels is predominantly carried out with aggressive solutions composed of nitric acid HNO_3 and hydrofluoric acid HF, referred to as mixed acid [21–23]. Pickling with nitric acid alone would quickly lead to passivation of the stainless steel surface. HNO_3 and HF have different tasks: While the strong oxidant HNO_3 mainly reacts with the metal oxides and the chromium depleted metal layer, which results in the formation of Fe^{3+}, Cr^{3+} and Ni^{2+} ions, HF is a strong chelating agent that will form complexes with the generated Fe^{3+}, Cr^{3+} and Ni^{2+} ions. At concentrations > 40 g/l the fluoride complexes can precipitate [24]. Mixed acid pickling solutions are used at temperatures up to 60°C [25].

Up to the present, HNO_3-free pickling solutions are used to a minor extend, as the application range is limited and the pickling process is harder to control [26, 27].

Due to the chemical reaction, an enrichment of the pickling medium with detached scale particles, dissolved metal salts (bound acid), as well as a depletion of acid that can still react with metals (so called free acid) takes place. In this way, the pickling medi-

um loses its effectiveness and must be replaced or refreshed, although it still contains a significant amount of unspent acid [28]. The best pickling effect can be achieved within a range of 35 to 70% of the saturation concentration of the appropriate metal salts. **Table 2** depicts the typical concentration range of sludge, spent acid, and rinse water.

Table 2

Composition of waste streams from stainless steel rolling plants [29–31].

	Sludge	Spent acid	Rinse water
Fe	18 wt.%	28–45 g/l	0.5 g/l
Cr	40 wt.%	5–15 g/l	0.05 g/l
Ni	2.5 wt.%	3–10 g/l	0.02 g/l
F$^-$	0.5 wt.%	15–80 g/l	0.5 g/l
NO$_3^-$		100–180 g/l	1 g/l
Free acid		3 mol/l	0.02 mol/l

Precipitated metal salts as well as detached scale are dispersed in spent pickling solutions [2]. According to Ito et al. the particle size ranges from <0.5 µm up to 30 µm [33] and the concentrations of suspended solids is between 9 mg/L to 800 mg/L [34]. Measurement of the particle size distribution showed a time depending increase of the particle size (median value) from 9 to 53 µm. Accordingly, the sedimentation velocity amounts to ca. $3.1 \cdot 10^{-4}$ m/s [33].

Characterisation of the sludge particles revealed following composition [33]:

SS304: Mainly Fe_2O_3, $FeCr_2O_4$; the total Cr content was about 30 %.

SS405: FeO, $FeCr_2O_4$, Cr_2O_3; the total Cr content was about 40%.

Today, the disposal of spent acid and rinse water is still often done using precipitation neutralization with lime milk, a dispersion of solid $Ca(OH)_2$ in water. The generated neutralization sludge is dewatered in chamber filter presses and then dumped. The main disadvantages of precipitation neutralization are the loss of valuable metals as well as still active acid, and high costs of neutralization chemicals and disposal.

Regeneration

Up to 50% of the total acid purchased ends up in the waste products generated by pickling lines, such as metal oxide containing sludge, spent acids, acidic gases, and wastewater from rinsing processes [35]. These wastes must be treated to meet the respective environmental standards. Accordingly, acid regeneration technologies contribute to reduced operating costs and reduced environmental impact of pickling lines. They can be divided into partial and total regeneration of the components. Partial regeneration

denotes those processes, which aim at the recovery of the free acid only. These include diffusion dialysis, electrodialysis, crystallization, and acid-retardation.

Total regeneration denotes those processes that aim at the recovery of both, free acid and bound acid. The technical and economic suitability of a specific partial or total regeneration process depends on the type of acid and the amount of pickling acid to be treated.

For the treatment of nitric / hydrofluoric acid containing pickling solutions, diffusion dialysis, retardation, and pyrohydrolysis are of particular technical relevance. The advantages and disadvantages, as well as any development prospects of this processes are briefly described below.

In the recent past, several reviews have been published with focus on the treatment of spent acidic solutions in the metal finishing industry [36] or on spent pickling solutions from steel processing [30]. Agrawal and Sahu [36] only focus on the treatment of different acidic waste solutions containing hydrochloric acid and sulfuric acid. Regel-Rosacka [30] considers the 3 most important steel pickling solutions. However, she makes errors in the description of the characteristics of regeneration methods. E.g., she wrongly denotes retardation as a process for metal recovery. Actually, a direct recovery of the acids is possible with retardation, while dissolved metals are transferred into the by-product. Metal recovery from the byproduct would be feasible only with additional technology. Furthermore, she stresses that pyrohydrolysis (spray roasting) serves for acid recovery only. In fact, pyrohydrolysis is a process for the total recovery of both, free acids and metals dissolved in spent acid (bound acids). And pyrohydrolysis is only one part of a process chain.

1. Pre-Treatment

To prevent blocking or mechanical damages of subsequent treatment steps as well as blocking of the pickling tanks, the suspended solids must be removed continuously from the pickling solution. Today, mainly four technologies are industrially applied, namely

- Sedimentation in external sedimentation tanks or lamella clarifiers. Sedimentation is affected by the high specific liquid gravity of the solution and convection currents due to the high temperature. Another specific disadvantage of sedimentation is the high water content of the slurry withdrawn from the bottom of the sedimentation tank [34].

- Multi-media filters, which can be used to re-

move particles up to 1 µm. For the application in acid recovery, the applied filter material must be resistant to chemical attack. Multimedia filters consist of at least two layers, a coarse particulate material serves for the removal of the multitude of suspended solids, and a finer layer which serves for the removal of traces of suspended solids. During operation, the suspended solids accumulate in the filter material, which leads to an increasing pressure drop. Accordingly, the filter must be backwashed. Generally, operating costs of multimedia filters are low, because the filter media does not need to be replaced [34, 37].

- Cartridge filtration using filter clothes. The feed is pressed perpendicular through the filter cloth surface, thus the rejected particles build up a dense filter cake, which acts as a separate filter medium with a small cut-off. According to the resulting flux decline or pressure, the cartridge filter is backwashed with compressed air or with a mixture of filtrate and compressed air [38].

- Microfiltration. With a membrane cut-off of 0.1–0.2 µm about 99% of the particle load of typical pickling solutions be removed. Microfiltration results in a particle free filtrate (permeate) stream and a retentate stream (suspension), which contains nearly all of the removed particles. The maximum concentration of particles in the retentate is restricted due to the density of the generated suspension [39–41].

2. Partial Regeneration

With the help of partial regeneration, the consumption of fresh nitric and hydrofluoric acid, can be significantly reduced. However, metal containing waste solutions are generated, which have to be treated. All in all, partial regeneration has a positive impact on the operating costs of pickling lines and on the environment.

According to literature, the most important partial regeneration processes for spent stainless steel pickling solutions are diffusion dialysis and retardation. Other processes which are often mentioned are electrodialysis (ED) and nanofiltration (NF) and extraction. However, these processes have never been used as single plants in large rolling mills.

2.1. Diffusion dialysis

Diffusion dialysis (DD) for acid recovery is a membrane separation process, the driving force of which is a concentration gradient on either side of special anion exchange membranes. The membrane stack consists of a multitude of compartments formed by anion exchange membranes, which allow acids to permeate from the spent acid solution into a clean phase, but which retain dissolved metals due to their charge and the selectivity of the membrane. The depleted feed (dialysate) leaves the upper part of the stack as an effluent containing high concentrations of metal salts and a low concentration of remaining acid [42].

With DD about 80–90% of the free acid from nitric acid containing spent pickling solutions can be recovered, the metal rejection is between 71% [43] and 93–97% [44]. The total amount of wastewater cannot be reduced with DD, as about 1 m³ of spent acid generates about 1 m³ wastewater [45].

The separation behavior of a DD membrane can be influenced by different operating parameters, such as flow velocity, feed concentration, temperature and differences in hydrostatic pressure between diffusate and dialysate. Fluoride has a stronger affinity to iron in the complexed compounds of the mixed acid and gradually replaces nitrate. Thus, a nitric acid recovery of > 100 % becomes possible [46, 47]. Furthermore, these effects can be explained by the concentration depending diffusivity of HNO_3 through the membrane [47].

Kun et al. [48] investigated diffusion dialysis on lab scale for the recycling of spent pickling liquors based on nitric acid. They observed that acid recovery rate decreased with the increase of feed flow rate and acid concentration. The acid recovery rate was more than 80% and metal rejection was more than 95% at equivalent volume flows of feed and water.

2.2. Retardation

Generally, acid retardation is a fully automated process comprising two major steps: In the first step, spent pickling solution is passed through a resin bed consisting of strongly alkaline anion exchangers, which adsorb the contained acid, while the remaining de-acidified metal salt solution – referred to as byproduct – leaves the resin bed. The byproduct forms a waste stream, which needs to be treated. As soon as the adsorption capacity of the resin is exhausted, the second step is started: The acid bound to the resin is released with desalted water due to osmotic pressure differences. Afterwards, the described cycle is repeated. Typically, the total cycle comprising acid adsorption, acid desorption and solution displacement last between 3 and 5 minutes. The total volume of the waste solution is not reduced. Similar to diffusion dialysis 1 m³ of spent acid generates about 1 m³ wastewater [20, 49].

With the help of retardation, about 98% of nitric acid and 80–90% of the fluoric acid could be recovered, metal removal was 80–90% [49].

2.3. Electrodialysis

Electrodialysis (ED) is a membrane process for the enrichment of charged substances (here: metals, protons, nitrate, fluoride) in aqueous solutions applying ion-selective membranes - alternating anion exchange membranes AEM and cation exchange membranes CEM – in an electric field The electrodialysis module consists of alternating anion-selective and cation-selective membranes (ion exchange membranes) which are separated by so-called spacers. Under the influence of a direct current electric field the anions are transported through the anion exchange membranes and the cations are transported through the cation exchange membranes, while the respective ions are rejected by membranes with the same charge. Thus, in adjacent chambers alternately a concentration and dilution occurs. Electrodialysis allows both, the recovery and concentration of acids and the separation of metals from a solution. The recovery of nitric acid is about 80%. Industrial-scale investigations showed that the nitrate content in the wastewater generated as a byproduct of retardation or diffusion dialysis could be reduced by 55% [50–52]. However, recovery of the costly hydrofluoric acid was only about 5 %-10 %. This is explained by the formation of undissolved HF and a multitude of complexed salts with different electric charges [53–56].

To prevent damage of the membrane stack, fluoride resistant electrodes have to be used. ED is not suitable for the direct treatment of spent acids, as – due to Faraday's law – the applied power is proportional to the intended concentration difference between feed and product. However, ED can be used to further decrease the nitrate content of retardation byproduct or diffusion dialysis dialysate. In the European stainless steel industry, there are 2 large-scale electrodialysis plants in operation, which help to reduce the eutrophication of the receiving waters [57].

A variation of conventional ED is electrodialysis with bipolar membranes (EDBM), which can be used to convert dissolved salts into their corresponding acids and bases, as bipolar membranes promote water splitting. The membrane stack consists of bipolar membranes in conjunction with conventional cation and anion exchange membranes. EDBM requires an applied current density between 500 and 1500 A/m^2 [58]. The industrial-scale application of EDBM is shown in chapter 2.3.

Negro et al. [59] describe a two-stage process for the treatment of a stainless steel pickling acid based on HNO$_3$ and HF. In the first stage, diffusion dialysis serves for the recovery of about 97% of HNO$_3$ and 50% of HF. While the diffusate is fed back to the pickling line; KOH is fed to the dialysate, which is acid depleted and contains nearly all of the dissolved metal salts of the initial solution, forming metal hydroxide sludge. The sludge is separated from the neutralized solution and drained. The neutralized solution is split in an EDBM plant into mixed acid - which is fed back to the pickling bath - and base solution – which serves for neutralizing the DD dialysate.

Disadvantages of bipolar ED are especially the high energy demand, as the current density is comparedly high (about 100 mA/cm²) and proton permeation through the bipolar membranes.

2.4. Extraction

Solvent extraction is a separation technique based on the partition equilibrium of substances between two immiscible liquid phases - an aqueous phase (spent acid) and an organic phase composed of an extractant and an organic solvent. Basically, extraction is divided into 3 steps:

- Mass transfer of the desired component from the initial aqueous to the organic phase (extraction)
- Removal of impurities from the organic phase into the aqueous phase (scrubbing)
- Mass transfer of the desired component from the organic phase to another aqueous phase (re-extraction or stripping) in order to recover the extractant.

The initial aqueous phase depleted of the desired component is referred to as raffinate.

3. Total regeneration

A major limitation of partial regeneration processes is that they can only recover free acids, while a significant part of hydrofluoric acid and the dissolved metals cannot be recovered since they are lost as metallic fluoride salts in the waste solutions that must be treated by neutralization-precipitation to meet the respective legal limits. Thus, several processes were developed with the aim to recover both, free and bound acid.

3.1. Pyrohydrolysis

The most important total regeneration processes in terms of installed plants are based on thermal processes, namely pyrohydrolysis, which is based on several high temperature chemical reactions [60], s. **Table 3**.

In the high temperature reactor, the metal salts are transferred into solid metal oxides, the respective respective acids are transferred to the gaseous phase. Accordingly, they need to be recovered from the flue gas of the reactor in absorption col-

umns. Drawback of pyrohydrolysis is the decomposition of a part of the nitric acid leading to the formation of NOx [61]. In a downstream oxidation column these NOx gases are converted into HNO_3. Thus, the total recovery rate is increased substantially [60]. However, remaining NOx in the exhaust gas must be eliminated by catalytic treatment (denitrification) which results in the formation of harmless N_2 [62].

For the pyrohydrolytic regeneration of spent pickling solutions containing HNO_3 and HF, two basic reactor principles are applied, spray roaster and fluidized bed reactor [63]. The Austrian company Andritz provides the spray roaster concept (Pyromars), the German company Steuler provides the fluidized bed technology with integrated downstream nanofiltration to achieve a higher HNO_3 recovery (STAR process) [64]. CMI UVK provides both, spray roasters and fluidized bed reactors. Spray roasters and fluidized bed reactors especially differ in size and quality of the generated oxides. Thermal regeneration processes allow the recovery of up to 99% HF and up to 90% of HNO_3, if nanofiltration is applied prior to the thermal processes. Up to 99% of Fe, Cr and Ni are recovered in the generated oxide, which can be reused in the steel smelting process.

Due to the higher recovery rate of the expensive fluoric acid, pyrohydrolysis can be a more economic option compared to retardation. The disadvantage of the thermal processes is the considerable technical and financial effort for installation and operation. Thus, economic operation of pyrohydrolysis is only feasible for spent acid volume flows > 0.3 m³/h or a required metal discharge of about 100 kg/h [64].

Spent acid is not the only acidic wastewater that is generated during pickling. Due to carry over of pickling acid into the subsequent rinsing zones of pickling lines, the rinsing water quality decreases. Andritz invented the ZEMAP process for the treatment of spent rinsing water as an addition to the PYROMARS process. Spent rinsing water is neutralized by ammonium in a first step, which results in the formation of soluble ammonium salts, such as NH_4F and NH_4NO_3. The neutralized solution is fed to the pyrohydrolysis reactor as well. The ammonium salts decompose under the given process parameters and the metal salts form metal oxides [60].

3.2. Kawasaki Process

The Kawasaki process was initially invented by Nisshin Steel Corp. Kawasaki Steel developed it further and in 1982 they commissioned an industrial-size regeneration plant with a capacity of 24 m³/day spent acid at their Chiba site. Basically, the process comprises following stages, s. **Table 4**:

In a first step, Fe^{3+} is selectively extracted from the spent pickling acid using 30% D2EHPA and 70% n-paraffin (in table 2 the extractant is abbreviated as HR). During subsequent stripping, Fe^{3+} extracted in the organic phase reacts with NH_4HF_2 (aq) and forms a ferric ammonium fluoride complex $(NH_4) FeF_6$ in the aqueous phase, which precipitates as crystals. These crystals are decomposed at about 500°C and form solid Fe_2O_3 and gaseous fluoride, which is removed from the flue gas by absorption. The iron depleted spent acid (raffinate of the 1st extraction) is mixed with HCl. Thus, nickel and chromium chloride is formed and HNO_3 is released. In a next step, HF and HNO_3 are extracted from the resulting solution using 70% TBP and 30% n-paraffin. From this organic phase, the mixed acids are stripped by water and can be recycled back to the pickling line. The acid depleted, metal salt enriched solution (raffinate of the 2nd extraction) is neutralized, this causes metal hydroxide precipitation. The hydroxides are separated and mixed with sulfuric acid. Then, they undergo a chemical conversion, during which mixed metal oxides are generated that can be re-used. Iron extraction of the process was about 95%, nitric acid recovery was about 95%, and hydrofluoric acid recovery was about 70% [65].

3.3. OPAR-Prozess

Outokumpu's acid recovery process (OPAR) was developed for a capacity of 1.4 m³/h spent acid and was commissioned in their Tornio site in 1985. In a first process step concentrated sulfuric acid (80–85%) is added to the spent mixed acid at an elevated temperature of 160–180°C. This leads to the precipitation of metal sulfates. The solution is fed to a vacuum evaporator, where HF and HNO_3 are separated from the remaining solution. The metal salts are afterwards removed by fractionated precipitation. The recovery of nitric acid and hydrofluoric acid is 95% and 99%, respectively [66].

3.4. Allied Signal Corp. process at Washington Steel

Washington Steel implemented a regeneration system based on bipolar electrodialysis (EDBM) supplied by Allied-Signal Corp., s. **Table 5**.

Table 3

Simplified reactions of pyrohydrolysis processes, after [60]

Process step	Unit operation	Reaction
Reactor	Evaporation	H_2O (l) → H_2O (g) HNO_3 (aq) → HNO_3 (g) HF (aq) → HF (g)
	Chemical conversion	$FeF_3 + 3\,H_2O → Fe_2O_3 + 6\,HF$ $CrF_3 + 3\,H_2O → Cr_2O_3 + 6\,HF$ $NiF_2 + 3\,H_2O → Fe_2O_3 + 6\,HF$ $2\,HNO_3 → NO_2 + NO + O_2 + H_2O$ $NO_2 ↔ NO + 1/2\,O_2$
Acid adsorber	Absorption	HNO_3 (g) → HNO_3 (aq) HF (g) → HF (aq)
Oxidation column	Chemical conversion	$NO + 1/2\,O_2 ↔ NO_2$
Catalytic de-nitrification (Denox)	Chemical conversion	$2\,NO_2(g) + O_2 + 4\,NH_3(g) ↔ 3\,N_2(g) + 6\,H_2O(g)$ $4\,NO(g) + O_2 + 4\,NH_3(g) → 4\,N_2(g) + 6\,H_2O(g)$

Table 4

Simplified reactions of the Kawasaki Steel process,
after [65]

Process step	Unit operation	Reaction
Iron separation from the spent acid	Fe Extraction	$FeF_2^+ + \overline{3HR} → \overline{FeR_3} + H^+ + 2\,HF$ $FeF_2^+ + \overline{HR} → \overline{FeF_2R} + H^+$
	Fe Stripping	$\overline{FeR_3} + 3\,NH_4HF_2 → \overline{3HR} + (NH_4)_3FeF_6$ $\overline{FeF_2R} + 3\,NH_4HF_2 → \overline{HR} + (NH_4)_3FeF_6 + 2\,HF$
Iron oxide formation from the crystals generated after stripping	Thermal decomposition at about 500 °C	$(NH_4)_3FeF_6 + \dfrac{3}{4}O_2 → 3\,NH_4F + \dfrac{3}{2}F_2 + \dfrac{1}{2}Fe_2O_3$
	Absorption	$2\,F_2 + 2\,H_2O → 4\,HF + O_2$
Acid recovery from the iron depleted solution (raffinate of the 1st extraction)	Chemical conversion	$Cr(NO_3)_3 + 3\,HCl → CrCl_3 + 3\,HNO_3$ $Ni(NO_3)_2 + 2\,HCl → NiCl_2 + 2\,HNO_3$
	Acid extraction	$HNO_3 + \overline{TBP} ↔ \overline{HNO_3 \cdot TBP}$ $HF + \overline{TBP} ↔ \overline{HF \cdot TBP}$
	Acid stripping	$\overline{HNO_3 \cdot TBP} ↔ HNO_3 + \overline{TBP}$ $\overline{HF \cdot TBP} ↔ HF + \overline{TBP}$
Ferrite formation from the iron and acid depleted solution (raffinate of the 2nd extraction)	Neutralisation	$(3 - x - y)Fe^{2+} + xCr^{3+} + yNi^{2+} + (6+x)OH^-$ $→ Ni_yFe_{3-x-y}Cr_x(OH)_{6+x}$ $H_2SO_4 + 2\,NaOH → Na_2SO_4 + 2\,H_2O$
	Chemical conversion	$Ni_yFe_{3-x-y}Cr_x(OH)_{6+x} + \left(\dfrac{1}{2} - \dfrac{x}{4}\right)O_2$ $→ Ni_yFe_{3-x-y}Cr_xO_4 + \left(3 + \dfrac{x}{2}\right)H_2O$

HR = extractant comprising D2EHPA and n-paraffin

overbars denote components in the organic phase

TBP = tributyl phosphate

Table 5

Simplified reactions of the Allied Signal Corp. EDBM Process at Washington Steel [67]

Process step	Unit operation	Reaction
Neutralisation of spent acid	Chemical conversion	$2\,KOH + HF + HNO_3 \rightarrow KF + KNO_3 + H_2O$
		$FeF_3 + 3\,KOH \rightarrow Fe(OH)_3 \downarrow + 3\,KF$
		$CrF_3 + 3\,KOH \rightarrow Cr(OH)_3 \downarrow + 3\,KF$
		$NiF_2 + 2\,KOH \rightarrow Ni(OH)_2 \downarrow + 2\,KF$
EDBM of the neutralized solution	Electro chemical conversion	$KF + H_2O \rightarrow KOH + HF$
		$KNO_3 + H_2O \rightarrow KOH + HNO_3$
Conventional ED of the EDBM diluate	Concentration / dilution	

In an initial step, spent acid is mixed with KOH to promote neutralization of the solution, and to release fluoride from bound acid. This way, metal hydroxides are generated which precipitate, while KF is dissolved. After separation of the hydroxide particles, the neutralised solution is fed into a 3 chamber EDBM that is operated batch wise in order to achieve a high efficiency. In the EDBM stack, the KF containing solution is split into KOH and mixed acid, while the initial solution is depleted (diluate). The generated mixed acid is fed back to the pickling line, while the generated KOH serves for neutralizing the spent acid. The EDBM diluate is then treated in a conventional ED to recover a higher concentrated KF solution that is also fed to the EDBM feed. The ED diluate is used for rinsing the filtered hydroxide sludge. The whole process aims at closed loops of the respective solutions. Between 1989 and 1990 about 1.5 Mio. Gallons/year of spent pickling acid were processed and about 90% of the employed acids could be recovered. This led to a ROI < 3 years [67].

Summary

In the production chain of stainless steels, pickling is a particularly quality determining step. Pickling with aqueous acid solutions comprising HNO_3 and HF has the largest industrial relevance. During the pickling process, a portion of the scale layer and parts of the base metal are dissolved and form metal salts, the concentration of which increases gradually in the pickling solution. At the same time, the concentration of the free acid decreases. Both effects lead to a decrease of pickling efficiency, so that upon reaching a certain concentration of dissolved metals the pickling bath must be regenerated or discarded. This entails a comprehensive sewage or concentrate treatment. Several commercial processes based on either the recovery of acid or the total recovery of acids and dissolved metals are available.

Their application depends on country-specific conditions, such as energy costs or the infrastructure for further processing of the recovered metal oxides.

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ИНФОРМАЦИЯ О СТАТЬЕ НА РУССКОМ

СТОЙКАЯ НЕРЖАВЕЮЩАЯ СТАЛЬ. ОБЗОР СИСТЕМ РЕГЕНЕРАЦИИ КИСЛОТЫ ДЛЯ ПРИМЕНЕНИЯ В ЛИНИЯХ НЕПРЕРЫВНОГО ТРАВЛЕНИЯ

Рёгенер Ф.[1], Леднова Ю.А.[2], Андрианова М.Ю.[2], Леднов А.В.[3]

[1]Институт разработки химических процессов и проектирования производств, Кёльн, Германия
[2]Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Россия
[3]Магнитогорский государственный технический университет им. Г.И. Носова, Магнитогорск, Россия. E-mail: alednov@mail.ru

Аннотация. Стали проходят несколько этапов обработки, чтобы достичь желаемого состояния доставки. Свойства и качество нержавеющей стали в основном определяются качеством поверхности изделия. В высокотемпературных процессах, таких как отжиг, прокатка и ковка, на поверхности стали образуются окалины толщиной от 5 до 10 мкм, состоящие из оксидов и гидратов оксидов. Кроме того, под слоем окалины содержание хрома в сплаве истощается за счет диффузионных эффектов, что приводит к снижению химической стабильности. Таким образом, химическое удаление как слоя окалины, так и слоя, обедненного хромом, в процессах травления является фундаментальным шагом для достижения чистых и однородных поверхностей. Большинство сталей протравливают как минимум один раз, обычно несколько раз.

Сильные минеральные кислоты обычно применяются в качестве травильных сред. Для травления нержавеющей стали обычно используют смеси азотной и плавиковой кислот - так называемые смешанные кислоты. В результате химической реакции происходит обогащение травильной среды отслоившимися частицами окалины, растворенными солями металлов (связанной кислотой), а также истощение активной кислоты (свободной кислоты). Таким образом, травильная среда теряет свою эффективность и должна быть заменена или обновлена. Это приводит к значительным выбросам потоков кислых отходов, которые необходимо обработать в соответствии с правилами. Потоки отходов содержат значительное количество растворенных тяжелых металлов, нитратов и свободной кислоты. Обычно применяется нейтрализация осадков, однако это приводит к потере растворенных ценностей. Кроме того, образуется значительное количество нейтрализующего осадка, который необходимо утилизировать, поскольку он представляет собой опасные отходы. По экологическим и экономическим причинам следует избегать потери ценностей. По этой причине травильные средства постоянно регенерируются на современных линиях травления. Акцент может быть сделан только на извлечении кислоты – это называется частичной регенерацией. Или на комбинированном извлечении кислоты и металла – это называется полной регенерацией.

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