



Review

A review on methods of regeneration of spent pickling solutions from steel processing

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ARTICLE INFO

Article history:

Received 21 October 2009

Received in revised form 7 December 2009

Accepted 7 December 2009

Available online 16 December 2009

Keywords:

Spent pickling solution

Wastewater regeneration

Hydrochloric acid

Sulfuric acid

Nitric/fluoric acid

ABSTRACT

The review presents various techniques of regeneration of spent pickling solutions, including the methods with acid recovery, such as diffusion dialysis, electrodialysis, membrane electrolysis and membrane distillation, evaporation, precipitation and spray roasting as well as those with acid and metal recovery: ion exchange, retardation, crystallization solvent and membrane extraction. Advantages and disadvantages of the techniques are presented, discussed and confronted with the best available techniques requirements. Most of the methods presented meet the BAT requirements. The best available techniques are electrodialysis, diffusion dialysis and crystallization; however, in practice spray roasting and retardation/ion-exchange are applied most frequently for spent pickling solution regeneration. As “waiting for their chance” solvent extraction, non-dispersive solvent extraction and membrane distillation should be indicated because they are well investigated and developed. Environmental and economic benefits of the methods presented in the review depend on the cost of chemicals and wastewater treatment, legislative regulations and cost of modernization of existing technologies or implementation of new ones.

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1. Introduction

Steelwork plants in European Union (EU) produce 300,000 m³/year of spent pickling solutions (SPS) and 150,000 t/year is stored [1]. Pickling step is essential to ensure high quality surface of steel for further processing. Acid is used to remove scale from the surface containing oxides. Pickling solutions are considered spent when the acid concentration in them decreases by 75–85%, which is

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accompanied by metal content increase even up to 150–250 g/dm³ [2]. Spent baths must be dumped because the efficiency of pickling decreases with increasing content of dissolved metal in the bath. The SPS content depends on the plant of origin and the pickling method applied there. SPS from steel pickling in hot-dip galvanizing plants contain zinc(II), iron (mainly iron(II)), traces of lead, chromium and other heavy metals (max. 500 mg/dm³) and hydrochloric acid. Zinc(II) passes to the spent solution after dissolution of this metal from zinc(II)-covered racks, chains and baskets used for transportation of galvanized elements. Bad covered zinc layers are usually removed in another pickling bath. As a result, zinc(II) concentration increases even up to 110 g/dm³, while iron content can exceed even 80 g/dm³ in the same solution [2].

2. Composition of SPS

Spent pickling solutions come from pickling of various surfaces. The composition of pickling bath depends on the composition and thickness of the surface. Generally SPS can be divided into two groups:

- solutions left after mild steel pickling in hot-dip galvanizing plants,
- solutions left after stainless steel pickling in rolling mills.

The first group consists of hydrochloric acid, iron and zinc ions, while the second group contains more harmful acids: a mixture of hydrofluoric and nitric acid or sulfuric acid and its mixture with hydrofluoric acid or hydrogen peroxide, iron and other metal ions (mainly: Cr, Ni) – see Table 1. Sometimes sulfuric acid is used instead of nitric acid in pickling baths for stainless steel treatment to make the bath less aggressive. In the past, sulfuric acid was very often applied for pickling, however nowadays in most cases it is replaced by HCl because the latter ensures better surface quality and a superior finish, faster pickling resulting in increase in steel throughputs and more economical HCl regeneration [3]. As a result of stainless steel pickling with a mixture HNO₃/HF, nitric acid oxidizes iron, chromium and nickel, while fluorides form metal complexes stabilizing these metals. When the concentration of metals in the pickling bath exceeds 5%, fluoride complexes start

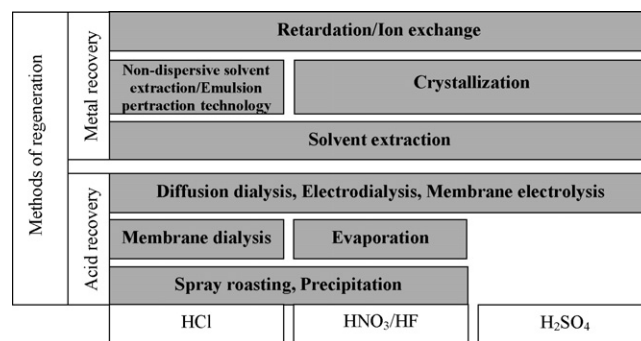


Fig. 1. General classification of SPS regeneration methods.

to precipitate. Then the spent bath is renewed and fresh acid is added. SPS from stainless steel pickling contains metal complexes, acids and free anions [4]. The methods of their regeneration should take into account various metal species formed in the SPS, such as zinc or iron chlorocomplexes or nickel, iron fluorocomplexes that affect the treatment of the spent liquor.

Compositions of exemplary real spent pickling solutions are presented in Table 1. Concentration ranges of acids and iron ions are very wide, which makes it difficult to select one universal method for SPS regeneration. Recovery of acids is an important economical issue; therefore methods enabling efficient removal and reuse of acids from SPS are still investigated and developed. Such methods must simultaneously allow effective removal of different metals such as: Cr, Ni, Cd, Zn, Pb. In all cases the metal ions mentioned are accompanied with high amounts of iron salts, which makes their efficient recovery a complex problem. Additionally, all SPS contain surfactants, inhibitors and stabilizers that are added to improve pickling effectiveness. Different physicochemical methods aimed at recovery are applied; in general they can be divided into two groups (Fig. 1): the methods enabling only acid recovery (such as electro dialysis, diffusion dialysis, membrane distillation, evaporation or spray roasting) and the methods enabling both metal and acid recovery (solvent extraction, retardation, ion exchange, crystallization). Recovery of metals and acids is a vital problem not only from the viewpoint of environment protection but also from that of

Table 1
Compositions of selected real spent pickling solutions.

Acid type	Acid conc., g/dm ³	Zn, g/dm ³	Fe, g/dm ³	Other	Ref.
H ₂ SO ₄	150	–	70	–	[8]
	92	–	78	–	[73]
HCl	237	~80	90–96 Fe(II), or 84 Fe(II), 8.3 Fe(III)	6.4 M Cl ⁻ , less than 400 ppm of Mn, Pb, Al, Cr, Ni, Cd, Cu, Co	[74–77,81]
	150	–	50	–	[8]
	101	–	8.9 Fe(III)	–	[13,14]
	90	80	30 Fe(II)	6 M Cl ⁻	[59]
	85	25	160 (158 Fe(II), 2 Fe(III))	Traces of Cd	[70]
	80	4.65	88.5 (incl. 1.6 Fe(II))	–	[42]
	~70	34	204	0.04 g/dm ³ Cr	[89]
	~40	110	88.5	7.7 M Cl ⁻	[71]
	33	12	106 Fe(II)	–	[38]
	20–60	–	80–110 Fe(II)	–	[3]
	18	26	140	0.09 g/dm ³ Pb, 0.08 g/dm ³ Ni, 0.03 g/dm ³ Cu, 0.09 g/dm ³ Al	[26]
	~10	70	92	–	[89]
	30	20	120	–	[46]
Mixed acids					
HNO ₃	180–200	–	28–30 (max. 35)	10–15 g/dm ³ Cr(III), 5–10 g/dm ³ Ni(II)	[56]
HF	40–45	–	30–45 Fe(III)	5–10 g/dm ³ Cr(III), 3–5 g/dm ³ Ni(II)	[4,8]
	120–150	–	–	–	
	15–30	–	–	–	
	125	–	40	–	[9]
30	–	–	–		

economy. Therefore, the aim of this paper is to present advantages and disadvantages of various methods of SPS regeneration with reference to the best available techniques (BAT) recommended by EU for metal processing industry. A review of the investigation and development in the recovery methods described since mid-1990s is given.

3. Hazards to the environment

According to the current legal acts accepted both in Europe and the USA [5,6] the concentration of metals and acids in wastewater should be strictly limited. The European and national standards give the permissible content of metals and chlorine ions in waste after neutralization as follows: 2 mg/dm³ Zn, 10 mg/dm³ Fe, 1 g/dm³ Cl⁻, pH 6–9. EPA regulations for steel pickling lines limit HCl concentration in the air to 6 ppm for continuous line and 18 ppm for batch pickling. Thus, regeneration of SPS is a crucial issue regarding both environmental protection and economy of the process.

Moreover, from the economical point of view, plants tend to reuse as much chemicals as possible, because unused or free acid in spent baths means the loss of chemicals and potential hazard to the natural environment. The ideal solution of the waste problem is application of a “near zero discharge” technology. All the streams in the process are recycled and utilized as much as possible, to produce no wastes and use up as little amount of fresh water and chemicals as possible. Secondary sources of materials are becoming increasingly important from the economic viewpoint and are of prospective use for future metal processing. Zinc recycling is a good example of secondary sources. Galvanization with zinc to protect steel elements from corrosion uses annually 70% of worldwide produced zinc (more than 7 million t/year); 30% zinc is recovered from secondary sources, mainly from furnace dust, spent pickling baths, spent batteries [7].

The term the “best available techniques” is defined in the European Council Directive 96/61/EC as “the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole.” It is clarified further that: “techniques” include both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned; “available” techniques are those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator; “best” means most effective in achieving a high general level of protection of the environment as a whole [5]. However, even when in some cases better emission or consumption levels can be achieved, the techniques are not considered BAT due to unprofitable economic calculus or cross media considerations.

Recovery and regeneration of acid from pickling step is recommended to limit the use of chemicals and emission of harmful gases to the air. Moreover, among other benefits the following must be listed [8]:

- better quality of products and reduced rework,
- increased average pickling speed,
- reduction in consumption of chemicals,
- increased environmental liability,
- compatibility with BAT recommendations (e.g., energy efficiency, reduction in air and water pollution).

4. Regeneration methods with acid recovery

4.1. Membrane techniques

The membrane techniques proposed to recover HCl and mixtures of HNO₃/HF, H₂SO₄/HCl or H₂SO₄/HNO₃ and HNO₃/HF include diffusion dialysis (DD) [9–12] and membrane distillation (MD) [13–19], electro dialysis (ED) with bipolar membranes [9,20,21], cation-exchange membranes [21,22], Neosepta membranes [23], and anion-exchange membranes [24] or membrane electrolysis (ME) [9,25–27]. Advantages and disadvantages of the membrane techniques used for SPS regeneration are collected in Table 2. Generally, membrane techniques are considered to be simple, effective and sustainable because of large and well-defined area of contact, compactness and reduced size of equipment, no need of chemicals addition, easy scale-up [28].

Both DD and MD processes enable recovery of HCl owing to counter-ion transport across the membrane and retention of metal salts. The difference in chemical activity of the acid on the two sides of the membrane is a driving force for the diffusion dialysis. The MD is driven by a partial pressure difference induced by temperature and composition of the layers adjacent to the hydrophobic, microporous membrane. Although DD is one of the cheapest membrane techniques, it enables separation of only Fe(II) from Zn(II). HCl recovered by this method is contaminated with Zn(II) that is transported together with the acid [12]. Despite its limitations DD is referred to as BAT because of low operating and maintenance costs, small apparatus and space requirements, low energy consumption, considerable reduction in fresh chemicals consumption and wastewater dumping, short amortization time. Previous filtration of used acids ensures long lifetime of membranes (3–5 years) and avoids their fouling [5,11]. As this method has been in use in Sweden for treatment of stainless steel pickling baths (HF/HNO₃), it is considered “available”.

MD is considered a highly selective operation for non-volatile solutions; however, Tomaszewska et al. provided evidence for its efficient application for recovery of volatile HCl [15,17]. The initial acid and Fe(III) concentrations in a model solution were changed from 18 g/dm³ to 250 g/dm³ and from 2 g/dm³ to 90 g/dm³, respectively [14]. Real solution used for MD studies contained nearly 9 g/dm³ Fe(III) and 100 g/dm³ HCl. Almost 100% FeCl₃ retention is obtained and the concentration of pure HCl in the distillate amounts to 100 g/dm³ [13–17]. Because of the presence of electrolyte, the salting out effect is observed in HCl solution, resulting in high molar flux of HCl through the membrane, and enhancement of HCl separation from the salt. No significant effect of the membrane material (PP, PTFE or PVDF are characterized in Table 3) or the module configuration on the final HCl concentration in the feed and distillate has been observed. MD is more energy-consuming than DD, however the recovery of HCl brings economical benefits, such as decrease in consumption of alkali used for neutralization of wastewater and separation of toxic metals. Unfortunately, selective recovery of metal ions from retentate by means of this method is not possible [15,16]. Despite the above-mentioned disadvantages, this method is regarded as a prospective technique for use in industry, and a flowsheet for MD treatment of metal pickling solutions is proposed (Fig. 2) [15,16]. Three steps of MD are assumed: the first one for concentration of SPS prior to crystallization, the second one for distillate concentration, and the third one for HCl recovery. Additionally, even up to 75% of energy can be recovered by heat exchange between the feed and the warmed distillate in countercurrent flow [18]. Fouling of the membrane in a long-time operation as well as concentration and temperature polarization must be emphasized as the main drawback of the membrane process. MD cannot be considered as “available” because it has been tested mostly on laboratory scale.

Table 2
Advantages and disadvantages of membrane techniques applied for SPS regeneration.

Method	Kind of SPS	Efficiency	Advantages	Disadvantages	Ref.
Membrane distillation	HCl, Fe(III)	Rec = 99.9% FeCl ₃	High selectivity for non-volatile solutes Use of waste heat or solar energy Recovery of pure water and pure HCl Separation of toxic metals	No recovery of pure metals Strong effect of feed composition on HCl recovery Flux decay due to membrane fouling in long-term operation Applied mostly on laboratory scale Concentration and temperature polarization High consumption of energy	[13–19]
Diffusion dialysis	HCl, Fe	Rec = 60% HCl Rec = 80% FeCl ₃	Extension of pickling bath life Elimination of waste disposal problems	Metal leakage across the membrane Double filtration necessary to prevent membrane fouling Consumption of fresh water	[10] [11]
Anion-exchange membrane (multiple)	HNO ₃ /HF H ₂ SO ₄ /HCl or H ₂ SO ₄ /HNO ₃ HNO ₃ /HF	Rec = 80–85% of free acid with 5% metal salt passage Rec = 97% HNO ₃ Rec = 50% HF	Regeneration and recovery of by-products Simple and easy maintenance The most energy efficient Unattended and continuous operation over a long time		[9]
Electrodialysis with bipolar membranes	HNO ₃ , HF, Fe(III), Cr(III), Ni(II)		Recycling of acid to the pickling bath Applied in industry Efficient recovery of acid and metal salts without any waste disposal Reduced consumption of chemicals Reduced waste volume and sludge	Membrane fouling by K ₂ SiF ₆ High investment cost High cost of membrane replacement	[9,20] [21]
Cation-exchange membranes	Acid, Fe or Zn, inhibitors and/or surfactants		Regulation of metallic impurity in the pickling bath Concentrated acid obtained Recovery of water	Poor selectivity of membranes Problem with leakage	[21,22]
Neosepta membranes	Model and real solution: HCl or H ₂ SO ₄ , Fe		Separation of acids from metal salts Very efficient method	For high water quality—additional mixed-bed ion exchanger necessary	[23]
Anion-exchange membranes	ZnCl ₂ , NaCl			Cannot be used for treatment of solutions containing HCl and Zn, because they form neutral and anionic chlorocomplexes	[24]
Membrane electrolysis	HCl, Fe, Zn		Depleting the solution of Fe, Zn, Cu, Ni, Pb	Chlorine gas formation – economic problem, undesired by-product (metal hydroxide)	[26,27]
Ceramic membrane	H ₂ SO ₄ , Fe	Yield of Fe powder 65–70%	Low production cost of ceramic membranes Regeneration of H ₂ SO ₄ and reuse Generation of iron powder as a product Reduced toxic wastewater and sludge discharge	No recovery of acid Membranes too sensitive to small particles (e.g., oil and grease) and to attack of chloride gas Low current efficiency Low corrosion stability of anode	[25]
	HF, HNO ₃ , Fe	Rec = 90% HNO ₃ Rec = 50% free HF	No fouling by K ₂ SiF ₆ (can be used for silica containing baths) Alternative to ED with bipolar membranes Reuse of water	Low resistance of electrodes to fluoride media Membrane electrolysis corrosion	[9]
Non-dispersive solvent extraction	HCl, Fe, Zn Real and model	E = 85–92%; S = 57–84%	Recovery of metals and chemicals “Near zero discharge” technology Recovery of valuable compounds Minimal impact on the environment Non-dispersion of the fluid phases High interfacial area Negligible extraction of iron Low maintenance cost No third phase formation as in classical SX No emulsification problems Effective removal of Zn	Low corrosion stability of anode Negative effect of membrane resistance on mass transport Aging of the membrane phase Limited efficiency due to small distribution coefficient of Zn between TBP and aqueous solution	[64,67–69, 74–78,81]

Rec – recovery; E – percentage extraction; S – percentage stripping

Table 3
Characterization of membranes applied in membrane techniques for acid and metal recovery.

Method	Membrane material	Membrane characteristics	Efficiency/recovery	Ref.
Membrane distillation	PP (Accurel)	$d_{in}/d_{out} = 1.8/2.6$ mm $d_p = 0.2$ μm (max. 0.6 μm) $\varepsilon = 73\%$ $A_{eff} = 110\text{--}120$ cm^2 Configuration: capillary module	$R_{\text{Fe(III)}} > 99.9\%$	[13–15,17,18]
	PTFE (Tarflen)	$d_p = 0.45$ μm $\varepsilon = 70\%$ $A_{eff} = 105$ cm^2 Configuration: flat-sheet	$R_{\text{Fe(III)}} = 99.5\%$	[13,18]
	PVDF	$d_p = 0.45$ μm $\varepsilon = 77\%$ $A_{eff} = 105$ cm^2 Configuration: flat-sheet	$R_{\text{Fe(III)}} = 99.5\%$	[13,18]
Electrodialysis	Bipolar membrane, ion exchange	Cationic: CMX Anionic: AHA-1 or AHA-2 Bipolar: BP-1 Configuration: 3-compartment cell stack	$\text{Rec}_{\text{HNO}_3/\text{HF}} = 95\%$ $\text{Rec}_{\text{KOH}} = 95\%$	[9]
Non-dispersive solvent extraction, emulsion pertraction technology	PP	Fiber $d_{in} = 240$ μm $\varepsilon = 40\%$ $A_{eff} = 1.4$ m^2 Configuration: HF module, Liqui-Cel Extra-Flow	$R_{\text{Zn}} = 42\text{--}94\%$ (depending on the membrane phase type) $R_{\text{Fe}} = 0\%$	[67–69,74–77,81]
Supported liquid membrane	Polidifluoroethylene	$d_p = 0.22$ μm $\varepsilon = 75\%$ $x_{\text{mem}} = 125$ μm	No data	[79]

d – diameter; d_p – nominal pore size of membrane; x_{mem} – thickness of a membrane, μm ; A_{eff} – effective area of membrane; R – retention coefficient; Rec – recovery; ε – nominal pore size, μm ; subscripts: in – inner, out – outer.

Electrodialysis of SPS is an effective way of acid recovery and wastewater purification [9,20–25]. This method enables not only separation of acid but also its concentration high enough to recycle the acid to be used in the pickling bath. Deacidified water can be used as rinsing water in the pickling step. Application of electrodialysis in a continuous work, as a part of industrial process to treat solutions containing HCl or H_2SO_4 , Fe and Zn ions, has been proposed and investigated by Paquay et al. [22]. However, the problem of undesired by-product formation (e.g., chlorine gas) should be solved, otherwise the membranes would be destroyed as they are sensitive to chlorine gas attack.

ED in the classical sense can be used to perform several general types of separations, while when slightly modified it is also used to produce acids and bases from the corresponding salts by forced water dissociation in bipolar membranes (composed of two different layers) [29]. ED is applied for regeneration of wastestreams (mainly HNO_3/HF from stainless steel pickling) neutralized with

base (e.g., KOH) to split the stream into acid and base. The acid recovered, resulting from ED or ME, is recycled to the pickling bath and the base to the precipitation step [9]. The water after ED is reused as rinsing water. Typical electrodialysis and bipolar membrane process differ in the water splitting characteristics of the bipolar membrane [5]. The main drawback of the bipolar membrane application is fouling by K_2SiF_6 , when silica is present in SPS. As the problem can be overcome using ME, this technique is likely to be more promising than ED. However, membrane corrosion and stability of the anode can be a problem and fluoride resistant electrodes should be used. When used for HCl regeneration, ME causes problems related to chlorine gas formation [27]. Energy consumption and investment costs (e.g., membranes used, feed flow velocity and pressure drop of the feed solution in the cell) affect the most the operation cost of ED [29]. Moreover, undesired sludge of metal hydroxide is produced. Despite the drawbacks, ED unit has been installed at the Outokumpu plant in Nyby to reduce the discharge of nitrates by nitric acid recycling, and to diminish by 50% fresh water and HNO_3 consumption [30,31].

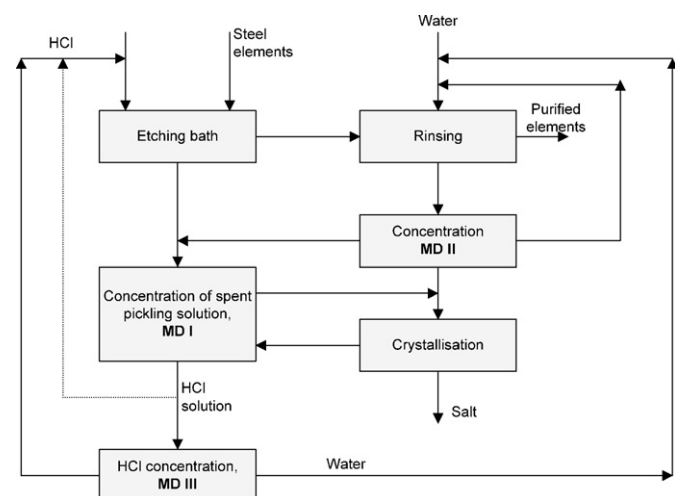
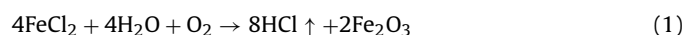


Fig. 2. The flowsheet of MD process for SPS solutions [15].

4.2. Pyrometallurgical techniques

Recovery of HCl from SPS with fluidized bed process (the so-called “Ruthner process”) or spray roasting is applied on the industrial scale in many plants in the world, and the scheme of the process is presented in Fig. 3. Hydrochloric acid is evaporated, and granules of iron oxides are formed in a fluidized bed at 800°C or in the spray roasting reactor at about 450°C [3,5,32,33] according to the following reaction:



After gas cooling HCl is condensed up to 200 g/dm^3 [5]. The acid is recycled to the pickling bath, while Fe_2O_3 is continuously removed in the form of granules, and can be used in steelworks. The pyrometallurgical method is unfriendly towards the environment (emission of exhaust gases), energy-consuming, and does not permit processing of solutions containing more than 0.5 g/dm^3

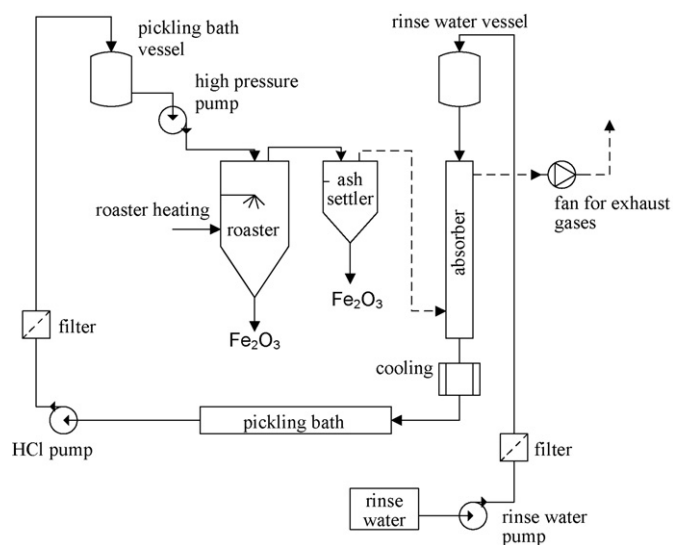


Fig. 3. Scheme of spray roasting process for SPS regeneration [5].

zinc(II), otherwise zinc disturbs the process, because it evaporates and sticks to the walls of the installation and contaminates iron oxides. The efficiency of acid recovery is very high (>99%) [34]. Metsep International has been using spray roasting installations in 200 steelworks around the world [33]. Iron oxide produced in the process is very pure and can be used for production of hard and soft ferrites, foundry applications, binder materials for refractories, coloring pigments. In small hot-dip galvanizing plants, the spray roasting is not practical – investment and operational costs are too high to compensate benefits from this method – while for large amounts of stainless steel SPS, this method is beneficial and widely applied.

Spray roasting has been also adapted for regeneration of mixed acids from stainless steel pickling (HNO_3/HF) and it is the so-called Pyromars process [5,35,36]. For this process the above-presented system is supplemented with the isothermal adsorption step and a tail-gas cleaning subsystem with a catalytic converter for NO_x . The SPS containing fluoride complexes of iron, chromium, nickel and free acids is pre-concentrated and then it is decomposed in the spray roasting reactor. After isothermal absorption the regenerated acid contains all of the free and bound hydrofluoric acid even up to 85% of HNO_3 . The regenerated acid is reused for pickling step [5]. The main disadvantage of this process is an expensive system for exhaust gas cleaning and the loss of 30–40% HNO_3 . Moreover, metal oxides are contaminated with fluorides.

Advantages and disadvantages of traditional methods of SPS regeneration are presented in Table 4.

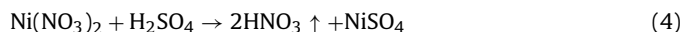
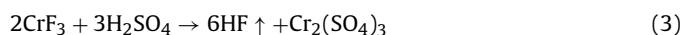
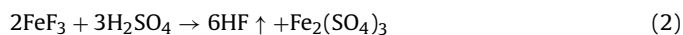
4.3. Precipitation/neutralization

Probably the oldest method proposed for SPS processing is precipitation [37] applied still in many, particularly small, hot-dip galvanizing plants. Waste from pickling stage is neutralized with lime (10–15% suspension) or NaOH/KOH . The method is simple, no complex installation is needed but it consumes a lot of chemicals. The precipitate of iron and zinc hydroxides, after sedimentation, is filtered and dumped in a landfill. The main drawback of this process is the cost of storage of the sludge. This method is limited by the growing need for landfills to store the precipitate. Moreover, no selective recovery of chemicals from the mixture of Fe and Zn hydroxides and neutral salts is possible [5,9,32,38,39]. Additional problem is very high-chloride content that prohibits further use of

the waste. Neutralization of SPS is not classified as meeting the BAT requirements.

4.4. Evaporation

Similar problems with salt fractions contamination with different zinc concentrations have to be faced when evaporation is employed. SPS, particularly HNO_3/HF , are concentrated with sulfuric acid (concentration up to 60%) at 80°C under vacuum according to the following reactions:



HNO_3 and HF driven off are condensed and reused in pickling step, while precipitated metal sulfates are neutralized with lime and are treated as hazardous waste. Although this method permits recovery of acid, it generates high investment and operating costs (because of the risk of corrosion, special high quality steel and fluorocarbon polymers must be used) [5,27,32]. Small changes in the fluoride and nitrate content in the recovered acid mixture are advantageous from the point of view of the process. Evaporation has been applied for mixed acid regeneration at the Outokumpu steelwork plant; the process is called the Outokumpu Pickling Acid Recovery (OPAR). Evaporation is also an important operation in Fluorex process patented in 1996 [40,41]. The process applies acid sorption technology to remove ferric sulfate and other metals from sulfuric acid. The system works at acid concentration lower than 50% w/w and the temperature lower than 90°C . The process is very efficient, and enables recovery of over 93% and 99% of fluoride and nitrate, respectively. Ammonia is employed to neutralize contaminants such as iron, chromium and nickel sulfate, and to recover their hydroxides. The ammonia then is regenerated by lime neutralization and steam stripping. Sulfate is recovered as a high purity gypsum cake.

In some cases precipitation/neutralization and evaporation are used as pretreatment techniques to diminish concentrations of metal salts prior to the proper method of SPS regeneration, especially combined with retardation.

5. Regeneration methods with metal recovery

BAT recommended by European Community and economic calculus have prompted the industry to search for such methods of SPS regeneration that would enable recovery of not only acids but also metal salts.

5.1. Ion-exchange resins/retardation

One of the simplest methods used for pickling liquor treatment is based on the use of ion-exchange resins for recovery of free HCl , H_2SO_4 , HNO_3/HF acids. This process is common in industry but produces a lot of diluted solutions.

Ion-exchange (IE) resins are used for recovery of pure salts [12,42–45]. Strong basic anion exchangers (e.g., Lewatit MP-500 macroporous, Lewatit M-504 gel, Lewatit VP OC 1071 gel) are used to retain metal chlorocomplexes that are next eluted with water. The method enables separation of Fe ions from both Zn(II) and HCl . Thus, three solutions are obtained as products: zinc chloride, iron chloride and HCl . The method is strongly limited by metal concentration in SPS, which cannot exceed 1 and $5\text{ g}/\text{dm}^3$ for zinc and iron, respectively [43]. Moreover, zinc chloride solution after IE is much diluted and must be concentrated prior to further use (e.g., in fluxing bath, for ZnCl_2 production). The costs of investment increase

Table 4
Traditional methods of SPS regeneration.

Method	SPS type	Efficiency	Advantages	Disadvantages	Ref.
Spray roasting	HCl, Fe, Zn HNO ₃ , HF, Fe(III)		Effective method for large amounts of SPS Reduced wastewater volume and sludge Operating costs are recovered by the value of the recovered acids and savings in neutralization costs Applied in industry	Limited by Zn(II) concentration High operational cost High consumption of fresh water and energy Complex installation High release of NO _x	[4,48]
Precipitation/ neutralization	HCl, Fe, Zn HNO ₃ /HF		Low operating costs Neutral sludge instead of acidic wastewater Simple technique and equipment Applied at small scale plants	Large consumption of chemicals Hazardous precipitation with high-chloride content No recovery of acid Expensive storage of the sludge High nitrogen content, does not meet the European Waste Treatment Regulations	[6,26,32,38] [9]
Evaporation	HNO ₃ /HF	Mixture of acids concentrated up to 60%	Recovery of HNO ₃ /HF Reduction of fresh acid consumption Small changes in the content of fluoride and nitrate in the mixture of acids No nitrates in wastewater No dust emissions Applied in industry	Metals are neutralized and form hazardous precipitation High investment and operating cost High energy consumption Consumption of additional acid (H ₂ SO ₄)	[5,27,32,40,41]
Retardation/ion- exchange	HCl, Fe, Zn HNO ₃ , HF, Fe(III)	Rec = 75–85% HF, Rec = 80–85% HNO ₃ , Rec = 50–55% metal salts	Effective retention of Zn in the resin Effective selectivity of Zn, Fe separation Low operation cost Little equipment and space Applied in industry	Production of high volume of waste Production of diluted solutions of metal salts High consumption of fresh water	[12,26,27,42–44]
Crystallization	HF, HNO ₃ , Fe, Cr, Ni H ₂ SO ₄ , Fe		Low cost Reduction of waste disposal Recovery of total amount of metals in a recyclable form Recirculation of HNO ₃ /HF mixture to the pickling process Reduced consumption of fresh acid	Bleeding out of acid containing high nickel concentration Risk of scale formation in a crystallizer Emissions to the air Increased consumption of energy	[4,48–52,55]
Solvent extraction	HCl, Zn, Fe		TBP is effective for wide range of Zn concentration in feed Good selectivity of zinc extraction over Fe(II) with TBP Acidic extractants permit Zn concentration up to 100 g/dm ³ after stripping High throughput with compact equipment	Organic impurities in the aqueous phase and extractant loss Adsorptive pretreatment is necessary to remove impurities Difficulties with stripping from Cyanex 923 and formation of stable emulsions Co-extraction of Fe(III) with Zn The greater the Zn concentration in the feed the higher the treatment cost	[27,32,38,56,59–66,79,80]
	HNO ₃ , HF, Fe(III)	$E_{Fe} = 91\%$, $E_{HNO_3} = 80\%$, $E_{HF} = 86\%$, selective stripping	High flexibility concerning Zn concentration in feed Continuous process with closed circuit Clean valuable product solutions Only physical separation	After long term of work third phase is formed Problems with phase separation after stripping Diluted strip solution–requires further treatment	[58]
	H ₂ SO ₄ , Fe(III)		Recycling of the recovered acid to pickling Can manage great volumes of solutions with a high content of toxic solutes		[73]

Rec – recovery; *E* – percentage extraction

also with increasing zinc concentration in SPS, because larger volumes of resins are necessary.

The Metsep process developed in South Africa applies three continuous countercurrent fluidized bed columns to separate zinc(II) over iron(II) in HCl prior to pyrohydrolysis. This continuous ion exchange provides the recovery of spent hydrochloric acid from the feed containing 20 g/dm³ Zn(II), 120 g/dm³ Fe(II), and 30 g/dm³ HCl. A special weak base anion-exchange resin is used with a specific gravity of about 1.2 g/cm³ (the feed solution density is 1.1 g/cm³). Selective separation of the chloride complexes of Zn(II) and Fe(II) in most recovery processes is based on the stability of their chloro-complexes. It is relatively easy to separate them since the latter do not form stable anion complexes at low acid concentrations. As the removal of zinc from the acid stream is achieved by ion exchange, Zn(II) can be recovered by SX using a cationic extractant (e.g., DEHPA – di-(2-ethylhexyl)phosphonium acid). Stripping from the organic phase is realized with H₂SO₄, thus zinc chloride is converted to zinc sulfate and can be applied as fertilizer additive [33,46].

Csicsovszki et al. propose a combination of anion exchange and membrane electrowinning techniques to recover HCl, and separate Zn from Fe [26]. The aim of these authors' investigation is to develop a technique that can be applied alone for the efficient treatment of SPS from hot-dip galvanizing plants. At first Zn contained in SPS is separated at anion-exchange resin (quaternary ammine type Polystyrene-DVB) and eluted with 0.1 M HCl. Acid and iron are recovered in the second step by membrane electrolysis (unfortunately the authors of [26] neither specify nor characterize the membrane type) with nickel electrode as a cathode. Zinc can be efficiently retained at the anion exchanger, while iron remains in the effluent. Then iron is deposited at the cathode at pH 1–1.5. However, the evolution of hydrogen at the cathode must be mentioned as a drawback of this method. This method still requires more detail investigation and optimization; however it seems to be prospective due to its simplicity.

On the other hand, anion-exchange resins (e.g., Lewatit VP OC 1071 gel) can be applied in acid retardation systems, where acid is retained in a column, and metal salts pass through the resin bed and are eluted from the column first as a waste or by-product. Recovery of HCl or H₂SO₄ amounts to 80–90% [5]. The method has been commercialized and applied as RECOFLO Acid Purification System and KOMParet Retardation System [8,42]. The drawbacks of the technique that should be mentioned include the processing of only small volume of solution in each cycle, poor selectivity and dilution of recovered solutions. On the other hand, the increased surface area and improved reaction kinetics, thanks to fine mesh resin beads, short and fixed resin beds to reduce the pressure drop, equipment size, finally countercurrent flows of the feed and regenerant to increase efficiency, make the process attractive and applicable in metal finishing industry [8].

APUTM (acid purification unit) continuous acid sorption system has been installed for recovery of mixed HNO₃/HF acids from pickling liquors, and seems to be more economically attractive than retardation of HCl and H₂SO₄ [8,45]. The recovery of free acid exceeds 95% and demand for nitric acid can be reduced by about 50% [47]. HCl retardation is attractive due to elimination of lost production time caused by bath dumping. When H₂SO₄ is used, SPS continuous retardation facilitates control of iron concentration (iron crystallizes out of sulfuric acid solution at content higher than 8 wt.%) [8]. Up to now the APU technology has been introduced in about 100 steel processing plants worldwide, however the stability of the resin in contact with nitric acid is of the major concern.

Dufour et al. [4,48–52] propose a combination of crystallization/precipitation and ion exchange to recover metals and acids from stainless steel pickling solutions. This process includes a mod-

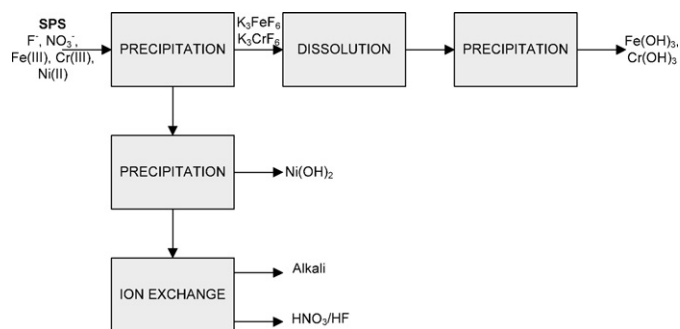
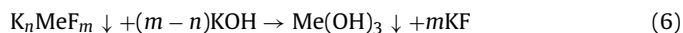
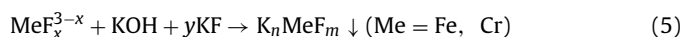


Fig. 4. Simplified block diagram of the modified crystallization/precipitation process.

ified precipitation of K₃FeF₆, K₃CrF₆ that are further dissolved and precipitated at higher pH as hydroxides according to the following reactions [4]:



At the same time Ni is precipitated as hydroxide, while diluted acids and alkali are formed after ion exchange from an effluent containing mainly potassium, nitrate and fluoride (Fig. 4). This process enables total recovery of metals in recyclable form and the mixture HNO₃/HF that can be reused in the pickling step. The authors hope that the process will be competitive to the established ones (e.g., Pyromars, Aquatech or OPAR processes) because of its low cost, minimization of waste disposal and recovery of both metals and acid mixture.

5.2. Crystallization

Crystallization is used for H₂SO₄ and HNO₃/HF spent pickling solutions and is based on the differences in the solubility of water, acid and iron salts. When using H₂SO₄ SPS, iron(II) sulfate heptahydrate is crystallized by indirect cooling crystallization, cyclone crystallization or vacuum cooling crystallization [5]. There is no need to neutralize free acid and iron, while pure salt is produced. Ozdemir et al. consider crystallization as an efficient method to remove ferrous chloride from hydrochloric SPS [53]. However, their studies are based on computer simulations and have not been verified in practice. Therefore in this review, crystallization is not considered as a method for regeneration of hydrochloric acid SPS.

Combination of two methods, nanofiltration and crystallization, has been investigated for the process of HF/HNO₃ regeneration in two stainless steel plants in Sweden [54,55]. Metals have been crystallized as fluoride salts (mainly FeF₃·3H₂O) that can form metal oxides after pyrometallurgical treatment. Pilot plant investigation has indicated some advantages such as reduced waste processing, reduced consumption of chemicals, reduced environmental impact at landfilling sites and downstream water treatment, along with some drawbacks such as out bleeding of acid containing high nickel concentration and increased risk of scale formation in crystallizer. This process is cost-saving and seems to be interesting for Swedish steelworks.

5.3. Classical and membrane based solvent extraction

The Kawasaki Steel Process using solvent extraction (SX) to remove iron from stainless steel pickling solutions was developed in the 1980s [56]. The process consists of four stages:

Table 5
Extractants used for regeneration of SPS in solvent extraction.

Extractant	Feed	Diluent/modifier	E, %	Remarks	Ref.
Acidic					
DEHPA (30%)	~30 g/dm ³ Fe, ~200 g/dm ³ HNO ₃ , ~45 g/dm ³ HF	n-paraffin	Fe: 95	Applied in Kawasaki Steel Process	[56]
DEHPA (40%)	<5–160 g/dm ³ Zn, HCl, Cu, Cd Co, Ni, Na as impurities	Kerosene	No data	Modified ZINCEX Process (MZP)	[84–86]
Cyanex 272	34 g/dm ³ Zn(II), 200 g/dm ³ Fe, 0.04 g/dm ³ Cr	Exxsol D 80	Zn: max. 70	Selective Zn extraction over Fe and Cr	[89]
Cyanex 301	2 M HCl	Exxsol D 80	Zn: max. 100	Selective Zn extraction over Fe and Cr even in very acidic solutions	[89]
Cyanex 302	34 g/dm ³ Zn(II), 200 g/dm ³ Fe, 0.04 g/dm ³ Cr, 2 M HCl	Exxsol D 80	Zn: ~10	Third phase formation, poor extraction	[89]
Solvating					
Cyanex 923 (30%)	0.5 g/dm ³ Zn, 0.58 M HCl, 5 M Cl ⁻	Exxsol D 220/230	Zn: 100	Inefficient Zn(II) stripping, third phase formation at high acidity	[60]
Cyanex 923	~1 g/dm ³ Fe(III), 2 g/dm ³ HNO ₃ , 0.05 M HF	Undiluted	Fe(III): 91	At first stripping of HNO ₃ /HF with water, than Fe(III) stripping	[58]
Cyanex 921 (30%)	0.5 g/dm ³ Zn, 0.58 M HCl, 5 M Cl ⁻	Exxsol D 220/230	Zn: 95	Third phase formation at high acidity	[60]
Cyanex 921 (0.2 M)	5 g/dm ³ Zn(II), 2 M HCl, 5 M Cl ⁻	Kerosene	Zn: 96	Inefficient stripping, oxidation of Fe(II)	[70]
TBP (30%)	5 g/dm ³ Zn(II), 110 g/dm ³ Fe(II), 2.5 M HCl, 5 M Cl ⁻	Decanol/kerosene (15/55 vol.%)	Zn: 96	Very good Zn(II) stripping with water, high selectivity over Fe(II)	[61]
TBP (1.1 M)	5 g/dm ³ Zn(II), 2 M HCl, 5 M Cl ⁻	Kerosene	Zn: 100	Good stripping with water	[63]
DBBP (80%)	50 g/dm ³ Zn(II), 0.58 M HCl, 5 M Cl ⁻	Exxsol D 220/230	Zn: ~80	Very good Zn(II) stripping with water, high selectivity over Fe(II)	[59,62,70]
ACORGA ZNX 50	36 g/dm ³ Zn, 60 g/dm ³ Fe mainly Fe(II), 50 g/dm ³ HCl and 4–6 M Cl ⁻	Varsol 10	Zn: >90	Strong dependence on water activity and total concentration of ionic species in the feed	[72,82,83]
Basic					
Amberlite LA-2 (30%)	5 g/dm ³ Zn(II), 2.5 M HCl, 5 M Cl ⁻	Exxsol D 220/230	Zn: 96	Good selectivity over Fe(III), formation of emulsions	[64]
HOE F 2562 (30%)	5 g/dm ³ Zn(II), 2.5 M HCl, 5 M Cl ⁻	Exxsol D 220/230	Zn: 94	Slow disengagement of phases	[60,61]
Alamine 336 (30%)	5 g/dm ³ Zn(II), 2.5 M HCl, 5 M Cl ⁻	Exxsol D 220/230	Zn: 99	Weak Zn(II) stripping	[60]
Aliquat 336 (30%)	5 g/dm ³ Zn(II), 2.5 M HCl, 5 M Cl ⁻	Exxsol D 220/230	Zn: 99	Poor selectivity over Fe(II), formation of emulsions	[61]

E – percentage extraction

- extraction of ferric ions (majority) with DEHPA in paraffins and stripping of iron by NH₄HF₂ as (NH₄)₃FeF₆ crystals,
- decomposition of crystals into Fe₂O₃ by heating,
- extraction of HNO₃ and HF with tributyl phosphate (TBP) in paraffins and stripping of acid mixture with water,
- formation of ferrite-type compounds of Ni and Cr from raffinate after HNO₃/HF extraction.

On the industrial scale the recoveries amounted to 95, 95 and 70% for iron, HNO₃ and HF, respectively.

Benedetto et al. [57] have proposed another approach to the recovery of HNO₃/HF, by SX. They added HCl or H₂SO₄ to form metal (Fe(III), Ni(II), Cr(III)) complexes that are not further extracted. HNO₃/HF are extracted with 70% TBP in isoparaffin, and then stripped with water. The technique is very effective, and allows recovery of 91% HNO₃ and 62% of HF. However, the authors have not mentioned metal ion co-extraction and have not proposed management of the metal salts. Another solvating extractant, Cyanex 923 (a mixture of phosphine oxides) can be successfully applied to recover Fe(III), HNO₃, and HF with high efficiency [58]. Co-extraction ($E_{Fe(III)} = 90.6\%$, $E_{HNO_3} = 80.3\%$, $E_{HF} = 85.7\%$) and selective stripping of iron(III), HNO₃, and HF with water prove that this method is suitable for SPS processing. Stripping for short time ensures very low Fe(III) content in the strippant, while the HNO₃ recovery is total; and the HF recovery, affected by the Fe(III) presence, is in the range accepted for HF recovery from SPS from stainless steels pickling.

The author's research group has been working on selective zinc recovery from hydrochloric acid SPS for a couple of years applying not only diffusion dialysis and retardation but also classical [59–66] and membrane based [64,67–69] solvent extraction (see Table 5).

Solvent extraction can be efficiently applied for Zn(II) separation from hot-dip galvanizing SPS. Some investigation on this subject was carried out in Germany leading to the construction of a mobile solvent extraction unit in the 1990s [27,32,38]. The unit uses TBP or DEHPA as extractants.

After screening for the most suitable extractant from among a wide spectrum of compounds (Table 5), TBP ($E_{Zn(II)} \sim 100\%$) and dibutyl(butyl) phosphonate (DBBP; $E_{Zn(II)} \sim 80\%$) have been selected for further examination [59,61,64,70]. The criteria of extractant suitability for SPS regeneration confirmed by Australian researchers [71] are as follows: good phase disengagement after extraction and stripping, high selectivity of zinc extraction over iron(II) and easy zinc stripping with water. The majority of basic extractants are not suitable for SPS regeneration due to formation of emulsions in contact with strongly acidic solutions. The authors propose a flowsheet of spent pickling solution recovery (Fig. 5) based on equilibrium studies [59–64] followed by extraction and stripping examination in mixer-settler units [65,66]. Some other

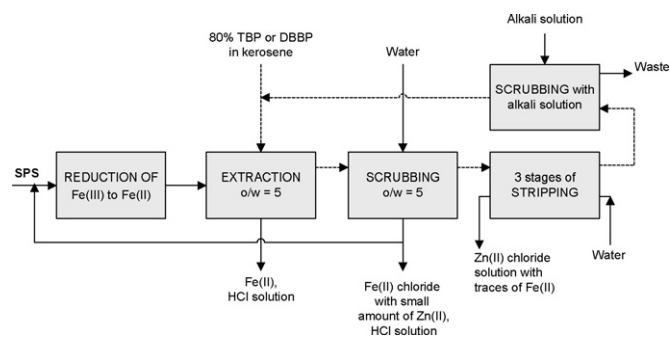


Fig. 5. Proposal of solvent extraction flowsheet for SPS treatment.

Table 6
Characteristics of SPS regeneration methods against BAT requirements.

Method	BAT requirement					
	Implementation in industry	Energy saving	Low emission of NO _x , CO	Reduced requirement of fresh chemicals and water	Reduction of wastestreams	Recycling of chemicals
Membrane electrolysis	–	+	+	+	+	+
Electrodialysis	+	+	+	+	+	+
Diffusion dialysis	+	+	+	+	+	+
Membrane distillation	–	–	+	+	+	+
Non-dispersive solvent extraction/emulsion pertraction technology	–	+	+	+	+	+
Solvent extraction	In the past	+	+	+	+	+
Spray roasting	+	–	–	+	+	+
Crystallization	+	+	+	+	+	+
Evaporation	+	–	–	+	+/-	+
Precipitation	+	+	+	–	+/-	–
Retardation/ion-exchange	+	+	+	+/-	–	+

authors studying TBP for zinc separation from iron(II) propose further treatment of stripping solution by evaporation of HCl after addition of excess sulfuric acid [72].

Extraction has been proposed for H₂SO₄ regeneration only by Agrawal et al. [73]. They propose quaternary ammonium salt Alamine 336 as an extractant to separate acid from Fe(III). As Alamine 336 strongly binds acid, the problem with incomplete stripping of H₂SO₄ from the organic phase appears.

The extraction-stripping process has been positively verified in the membrane based solvent extraction system. The membrane based extraction can be realized in the system of two modules with the organic phase circulating in the shell side of the modules [64,67–69,74–78] or in one module in which polymeric support is impregnated with the organic phase – SLM [79]. Zn(II) transport through supported liquid membrane (SLM) impregnated with 30% Cyanex 923 in Solvesso 100 is controlled by diffusion in the aqueous solution, and needs a long time. SLM seems to be rather laboratory equipment for preliminary studies and is not long term stable, which is probably responsible for the lack of its commercial success [80]. The final efficiency of the non-dispersive solvent extraction (NDSX) is limited by relatively small values of the distribution coefficient of zinc(II) between TBP and aqueous solution [67–69]. As a result at least several modules should be used to remove zinc(II) from wastewater. Selectivity of zinc separation over iron(II) changes from 30 to 125, depending upon the initial metal concentration in the feed [76,77]. The effective receiving phases are water and 1 M NaCl for NDSX and SLM, respectively. Membrane based NDSX seems to be competitive with classical SX because of low maintenance cost, non-dispersion of the fluid phase and the high interfacial area [74]. Additionally, the most recent studies have proposed emulsion pertraction technology (EPT) as an alternative to NDSX. The advantages of EPT are as follows: lower membrane area need for one membrane module and higher interfacial area. EPT combines emulsion containing extractant (TBP) and stripping phase (water) with zinc transfer from feed to emulsion in a single hollow fiber (HF) module [81]. Though estimated mass transfer coefficient is higher than for the NDSX method, overall zinc transfer to the stripping phase is lower.

Elimination of phase-separation problems is the main advantage of the membrane based extraction, even for systems with small difference in phase densities and low interfacial tension, due to the immobilization of organic phase in the membrane pores.

In the early 1990s some authors proposed dibenzimidazole based neutral extractant ACORGA ZNX 50 to recover Zn selectively over Fe, As, Ca, Cr, Pb, Mg, Mn and Ni from strongly acidic solution [82,83]. The extractant is highly selective for Zn over Fe and a range of other metals including Cd, As, Pb and Mg. The effective

zinc recovery from the galvanizing pickle liquor containing high Fe, HCl and Cl[–] concentrations (36 g/dm³ Zn, 60 g/dm³ Fe mainly Fe(II), 50 g/dm³ HCl and 4–6 M Cl[–]) is proved in a mixer–settler unit. Ninety percent of zinc is extracted in three stages while iron is left in the raffinate. The loaded zinc can be stripped with spent electrolyte or water in the close loop of solvent extraction and electrowinning circuit [72]. However, this extraction with ACORGA ZNX 50 is strongly dependent on water activity and concentration of species in the feed. Too high Cl[–] concentration reduces Zn extraction and this observation can explain little interest in application of the extractant on a larger scale.

Zincex and Modified Zincex Processes (MZP) have been proposed by Técnicas Reunidas to produce zinc salts and to recover acid from various secondary sources, among them spent pickling solutions [84–87]. DEPHA in kerosene is used as an extractant. Impurities such as Co, Ni, Cd, Mn are rejected by the extractant, while ultra-pure zinc sulfate is stripped from the loaded organic phase with spent electrolyte from the electrowinning cells. In 1980 in Portugal a plant for treatment of high-chloride leach liquors from various sources (Quimigal) was established on the basis of MZP allowing production of SHG (super high grade) zinc [85,86,88]. Additionally, other acidic extractants such as Cyanex 272 [bis(2,4,4-trimethylpentyl) phosphinic acid], Cyanex 301 [bis(2,4,4-trimethylpentyl) dithiophosphinic acid] and Cyanex 302 [bis(2,4,4-trimethylpentyl) monothiophosphinic acid] and solvating TBP are investigated to remove selectively zinc(II) over iron(II) [89]. Mansur et al. have confirmed the need for additional step of iron(III) reduction prior to extraction due to instability and degradation of dithiophosphinic acids in the presence of iron(III). The best selectivity of zinc(II) over iron(II) extraction is achieved with Cyanex 301 and TBP. The main drawback of TBP is the large volume of extractant necessary to recover zinc(II) efficiently, while the main drawback of the use of Cyanex 301 is related to its chemical instability.

Unfortunately, none of the installations using SX for regeneration of SPS is still working. As known, extraction is used for large-scale operations [80], SX seems not to be economically attractive enough to recover zinc from secondary resources; probably due to not large enough amount of liquors and rather periodic need for such a system or small installations using cheaper methods of regeneration. However, SX has a great advantage over the other methods: it is very flexible – it permits to process effluents of wide concentration range of metal ions.

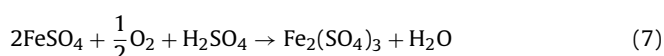
5.4. Other options

Direct conversion of HCl to FeCl₂ is proposed for hydrochloric acid SPS as a feasible process [53]. It is a simple and economic

solution in the case of demand for ferrous chloride. However, the main drawback of the method is the formation of explosive hydrogen gas during the conversion according to the following reaction: $\text{Fe} + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2$. These authors propose to use hydrogen to produce energy or to reduce Fe(III) to Fe(II) in the SPS.

A novel and promising method is the synthesis route from spent sulfuric acid pickling solution to ferrite nanoparticles, proposed by Konishi et al. [90]. The flowsheet proposed for H_2SO_4 (containing 40 kg/m^3 Fe(II) and pH 0) assumes the three following steps:

- Microbial oxidation of Fe(II) in sulfuric acid pickling solution:

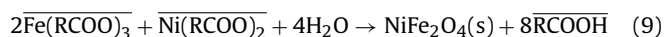


- Solvent extraction of Fe(III) in microbially oxidized solution with the monocarboxylic acidic extractant RCOOH (commercial Versatic 10):



where horizontal line denotes organic phase.

- Solvothermal synthesis (at 190°C) of nickel ferrite from the organic carboxylate solution of iron(III) and other metal (Ni(II)):



As a result crystalline nickel ferrite nanoparticles of 31 nm diameter are synthesized. Successful preparation of magnetite nanoparticles of 48 nm has been also carried out.

6. Summary

Generally, the recycling of HNO_3/HF mixtures is much better resolved and developed than recycling of HCl and H_2SO_4 because of great amounts of SPS from stainless steel pickling. There are more processes applied in industry around the world for regeneration of HNO_3/HF mixtures than for the recycling of hydrochloric acid SPS from hot-dip galvanizing. Neutralization by precipitation from SPS is not classified as BAT. The methods for H_2SO_4 regeneration are in minority because in most pickling baths sulfuric acid is replaced with HCl.

Most of the methods presented meet the BAT requirements, as shown in Table 6. Although only spray roasting or fluidized bed for HCl and mixed acids, crystallization for H_2SO_4 and IE, dialysis or evaporation for mixed acids are considered as BAT in the official IPPC document, there are more methods that are still under development, and finally they will meet BAT requirements. It is assumed that new installations can be designed to perform at the general BAT levels or even better. Obviously the existing installations could improve the general BAT levels [5]. The general classification does not consider all features of the methods presented. For example ED: despite no emission of CO or NO_x , chlorine gas is emitted, so special solutions are required to limit and control this process.

7. Conclusions

As the best available techniques ED, DD and crystallization should be pointed out. However, in practice the spray roasting and retardation/IE are applied in most cases for SPS regeneration. As “waiting for their chance” SX, NDSX and MD should be indicated because they are well investigated and developed. However, their applicability and feasibility depends on the quantity of SPS to be processed.

Obviously, to achieve a “near zero technology” not only effective regeneration methods must be implemented but also optimization of pickling steps should be carried out to reduce concentrations

of the metal ions (especially Zn(II)) as much as possible. Additionally, pretreatment of SPS prior to further regeneration treatment, e.g., crossflow microfiltration [35], can successfully improve performance of the recycling due to better quality of metal oxides and less downtime for cleaning the installations.

It must be emphasized that the processes with acid and metal recovery reduce waste volume to be discharged to the environment and generate sellable products such as iron salts (used as coagulants), iron oxides (pigments), zinc salts (used as fluxing agents or by-product for zinc oxide). Environmental and economic benefits of the methods presented in the review depend on the cost of chemicals and wastewater treatment, legislative regulations and cost of modernization of existing technologies or implementation of new ones.

Acknowledgment

This work was supported by the 32-067/10-DS grant.

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