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Methods of regeneration of spent pickling solutions from steel treatment plants

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Facing the still growing demand for metals, particularly for zinc, the recovery of metals from secondary sources should be considered. Spent pickling solutions can be the source of valuable products such as hydrochloric acid, zinc or iron salts or even metallic zinc. The selection of an efficient, selective and economical method for the regeneration of such solutions is a key issue for hot dip galvanizing plants, especially in reference to strict environmental protection regulations.

Keywords: spent pickling solutions, hot-dip galvanizing, waste regeneration, hydrochloric acid, zinc(II), iron.

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INTRODUCTION

Hot-dip galvanizing is widely applied to protect steel products from corrosion. The process consists of several steps, where good preparation of steel surface plays a crucial role. Pickling with acids removes non-metallic substances, such as rust and scale, from the surface providing the material of required purity. Moreover, poor zinc coatings are usually removed also in pickling baths. As a result, zinc(II) concentration in spent pickling solutions increases even up to 130 g/dm^3, iron content to 100 g/dm^3, HCl to 10%[1–3]. The composition of the waste depends upon a plant and the way of pickling applied, which is presented in Table 1.

Table 1. The composition of spent pickling solutions

Process	Zn, g/dm^3	Fe, g/dm^3	HCl, g/dm^3	Other, mg/dm^3	Ref.
	Germany				
Iron pickling	< 5	> 100	< 80	–	2
Mixed pickling	5 – 80	> 80	< 80	–	
Zinc pickling	> 130	<12.5% of Zn content	< 80	–	
	Poland				
Iron pickling	max. 3	min. 130	max. 70	Pb max. 100, Cr max. 500, other heavy metals max. 500	3
Zinc pickling	125	12.5	no data	–	

According to the European and national standards the permissible content of waste after neutralization is as follows: 2 mg/dm^3 Zn, 10 mg/dm^3 Fe, 1 g/dm^3 Cl^-, pH = 6 – 9. Thus, regeneration of spent pickling solutions is a crucial issue regarding both the environmental protection and the economy of the process.

It is the aim of the work to present the advantages and disadvantages of different methods for the regeneration of spent pickling solutions from hot dip galvanizing plants as a background for the results obtained in our group with solvent and membrane based extraction.

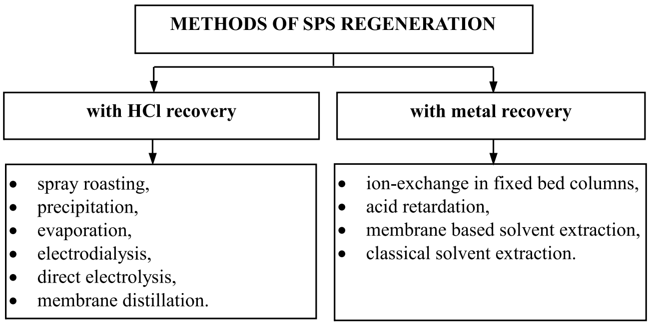


Figure 1. Magdalena Regel-Rosocka, Anna Cieszyńska, Maciej Wiśniewski, Methods of the Regeneration of Spent Pickling Solutions from Steel Treatment Plants

Depending on the composition of spent pickling solution (SPS) various methods of their regeneration are used. They are presented in Fig. 1. Some of the methods enable the recovery of only hydrochloric acid, while zinc and iron form a concentrated sludge which has to be stored. Facing the still growing demand for metals, particularly for zinc, the recovery of metals from secondary sources, such as SPS, should be considered.

REGENERATION METHODS WITH HCL RECOVERY

The recovery of HCl from SPS with spare roasting (the so called „Ruthner process") is applied on an industrial scale in about 80 plants in the world. Hydrochloric acid is evaporated and granules of iron oxides are formed in a fluidized bed at 800°C. After gas cooling HCl is condensed up to 200 g/dm^3 [4,5]. The acid is recycled to the pickling bath, while Fe_2O_3 is continuously removed as granules and can be used in steelworks. The pyrometallurgical method is unfriendly towards the environment, energy-consuming and does not permit to process solutions containing more than 0.5 g/dm^3 of zinc(II). In other case zinc can disturb the process, because it evaporates and glues to the walls of the installation.

In many, particularly small, hot dip galvanizing plants waste from pickling stage is neutralized with lime (10 – 15% suspension) or NaOH/KOH. The precipitation of iron and zinc hydroxides, after sedimentation, is filtered and dumped on a landfill. The main disadvantage of this

Table 2. Extractants used for the regeneration of SPS (Feed: Zn(II), Fe(II), 10% HCl; extractants were diluted in Exxsol D 220/230)

Extractant	$E_{Zn(II)}$, %	Remarks	Ref.
Amberlite LA-2 (30 vol.%)	96	Good selectivity over Fe(III), formation of emulsions	20
HOE F 2562 (30 vol.%)	94	Slow disengagement of phases	16, 17
Alamine 336 (30 vol.%)	99	Weak Zn(II) stripping	16
Aliquat 336 (30 vol.%)	99	Poor selectivity over Fe(II), formation of emulsions	17
Cyanex 923 (30 vol.%)	100	Weak Zn(II)stripping	16
TBP (100%)	96	Very good Zn(II) stripping with water, high selectivity over Fe(II)	17
DBBP (80 vol.%)	100	Very good Zn(II) stripping with water, high selectivity over Fe(II)	18

process is the cost of storage of the sludge. Moreover, no selective recovery of the chemicals from the mixture of Fe and Zn hyroxides and neutral salts is possible[6, 7]. Additional hazard results from a very high chloride content, which prohibits further use of the waste.

Similar problems of salt fractions contaminated with different zinc concentrations have to be faced when evaporation is employed. Although it permits the recovery of acid, it generates high investment and operating costs[6, 7].

Some membrane techniques were proposed to recover HCl, among them diffusion dialysis[8, 9] and membrane distillation[10, 11]. Both processes enable the acid recovery owing to counter-ion transport across a membrane and retention of metal salts. The difference in the chemical activity of the acid between the two sides of a membrane is a driving force for the diffusion dialysis. The membrane distillation is driven by a partial pressure difference induced by temperature and the composition of the layers adjacent to the membrane. Although diffusion dialysis is one of the cheapest membrane techniques, it makes it possible to separate only Fe(II) from Zn(II). HCl recovered by this method is contaminated with Zn(II) which is transported together with the acid[8]. Membrane distillation is more energy-consuming than diffusion dialysis, however the recovery of HCl brings economical benefits, such as decrease in consumption of alkali used for the neutralization of wastewater and the separation of toxic metals. Unfortunately, it is not possible to recover selectively metal ions from the retentate with this method[10, 11]. Despite the mentioned disadvantages it is regarded as a prospective technique for use in industry.

Electrodialysis of spent pickling solutions is an effective way of acid recovery and wastewater purification[12, 13]. This method enables not only the separation of acid but also its concentration, high enough to recycle the acid to the pickling bath. De-acidified water can be used as rinsing water in the hot dip galvanizing process. An 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, is proposed and investigated by Paquay et al.[12]. However, the problem of the undesired by-product formation (e.g.: chlorine gas) should be solved, in another case membranes would be destroyed, as they are sensitive to chlorine gas attack[6].

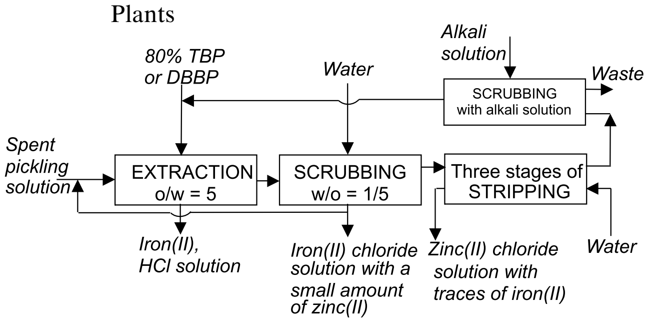
REGENERATION METHODS WITH METAL RECOVERY

Economic calculus and BAT techniques recommended by The European Community make industry look for such methods of SPS regeneration that enable to recover also metal salts. Separation of the pure salts is possible with ion-exchange resins[8, 14, 15]. Strong basic anion exchangers are used to retain metal chlorocomplexes which are next eluted with water. The method enables to separate 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 g/dm^3 for zinc and iron, respectively[15]. Moreover, zinc chloride solution is highly diluted and must be concentrated prior to further use (e.g.: in fluxing bath, for $ZnCl_2$ production). The costs of investment increase also with increasing zinc concentration in SPS, because larger volumes of resins are necessary then. On the other hand, anion-exchange resins 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. The method has been commercialized and applied as RECOFLO Acid Purification System and KOMParet Retardation System[14]. However, its main disadvantage is the problem of poor selectivity and dilution of waste solutions.

Our research group has been working on selective zinc recovery from SPS for a couple of years applying not only the diffusion dialysis and retardation but also the classical[16 – 22] and membrane based[20, 23, 24] solvent extraction.

Solvent extraction can be effectively applied for Zn(II) separation from SPS. Some investigations in this subject were carried out in Germany leading to the construction of a mobile solvent extraction unit in the 90s[6, 7, 25]. The unit applied tributyl phosphate (TBP) or di(2-etylhexyl)phosphoric acid (DEHPA) as extractants. In our laboratory after screening for the most suitable extractant among the wide spectrum (Table 2), TBP and dibutyl butylphosphonate (DBBP) have been selected for further examination. The criteria of extractant suitability for SPS regeneration 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 authors propose a flowsheet of spent pickling solution recovery (Fig. 2) based on equilibrium studies[16 – 20] followed by extraction and stripping examination in mixer-settler units[21, 22].

Figure 2. Magdalena Regel-Rosocka, Anna Cieszyńska, Maciej Wiśniewski, Methods of the Regeneration of Spent Pickling Solutions from Steel Treatment Plants



SPS is contacted in one step with 5 – 10 folded excess of 80% TBP. A raffinate after zinc extraction contains iron(II) and HCl, thus it can be used to produce coagulants for water treatment plants. The loaded organic phase contains high amounts of zinc and some of iron(II). The latter can be removed from TBP by scrubbing with a small volume of water. Scrubbings containing iron(II) with small amount of zinc should be recycled to a reduction step (to prevent the oxidation of iron(II) to iron(III)). The organic phase loaded with zinc is contacted with water to strip zinc. Before recycling, TBP should be washed with alkali solution to remove the products of hydrolysis, mainly dibutylphosphoric acid, and to hold back in this way the undesired transfer of iron(II) to the recycled TBP. Thus, losses of extractant to the aqueous phase are the main disadvantage of the proposed process. Additionally, the aqueous phase after stripping is diluted and contains zinc(II) and HCl, so it should be concentrated prior to further use. However, the method provides high throughput, high flexibility concerning zinc concentration and acidity in feed and clean products that can be recycled or sold.

The extraction-stripping process with TBP as an organic phase has been positively verified in the membrane based solvent extraction system containing two hollow fiber modules[20, 23 – 28]. However, the final efficiency of the process is limited by the relatively small values of the distribution coefficient of zinc(II) between TBP and the aqueous solution[23, 24]. 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[26, 27]. Elimination of phase-separation problems is the main advantage of the membrane based extraction, even for the systems with a small difference of densities and low interfacial tension, due to the immobilization of the organic phase in the membrane pores.

CONCLUSIONS

Two different ways of SPS treatment are applied. One leads to the recovery and reuse of HCl, while metal salt sludge is rejected as a waste, and the other enables not only to separate HCl but to reduce the amount of toxic zinc in the wastewater and to obtain $ZnCl_2$ solution, crystalline salt or metallic zinc. Taking into account the economical, environmental and technical advantages and disadvantages of the presented methods solvent extraction, both the classical and the membrane based, seems to be a good solution for a hot dip galvanizing plants.

Acknowledgement

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