REVIEW

Acid pickling of carbon steel

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ABSTRACT: This study reviews the possibilities of recovering the pickling waters from carbon and galvanised steel. Acid pickling with hydrochloric acid (HCl) is the most widely used chemical process to remove iron oxides from the metal surface without any significant attack on the steel itself. The acid pickling bath contains mainly ferrous chloride (FeCl\textsubscript{2}) produced by the reaction between the steel and free hydrochloric acid. However, zinc chloride (ZnCl\textsubscript{2}) is also found in the pickling of carbon steel parts prior to galvanisation, as the hooks and tools used to hang the carbon steel parts are also galvanised and reused again polluting with Zn the pickling waters. Pickling water recovery or recycling technologies primarily seek the reuse of HCl in two ways. Partially by recovering the unreacted HCl or fully by breaking the FeCl\textsubscript{2} bond through Pyrolysis technologies such as fluidized bed and spray roasting which in turn produces another iron oxide by-product. However, the most common by-product produced by pickling water recovery and recycling technologies is ferric chloride (FeCl\textsubscript{3}), as it is a coagulant widely used in wastewater treatment. However, if the pickling water contains ZnCl\textsubscript{2} or other metals, the production of FeCl\textsubscript{3} becomes unattractive and the pickling water is neutralised and deposited in landfill sites. This study also discusses a wide range of technologies capable of recovering all or part of the pickling water, including galvanic pickling water, that are usually excluded from circular economy strategies.

KEYWORDS: Hot dip galvanizing; Hydrochloric acid; Iron (II) chloride; Steel pickling; Zinc chloride

RESUMEN: Decapado ácido de aceros al carbono. Este estudio analiza las posibilidades de recuperación de las aguas de decapado del acero al carbono y galvanizado. El decapado ácido con ácido clorhídrico (HCl) es el proceso químico más utilizado para eliminar los óxidos de hierro de la superficie del metal sin que se produzca un ataque significativo al propio acero. El baño de decapado ácido contiene principalmente cloruro ferroso

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1. INTRODUCTION

Chemical pickling is an industrial process to remove the surface layer of iron oxides that are formed in steel products exposed to atmospheric oxidation or in the different stages of carbon steel production so that it can then be coated and protected from corrosion.

When carbon steel is heated to air at temperatures between 575 and 1,370 °C, oxides can be formed on its surface (Turgoose and Bullough, 2013) during the different stages of the steel production, for example during casting, forging, hot rolling and annealing. This oxide is commonly called husk and consists of three well-defined layers, the thickness and composition of which depend on the duration and temperature of heating. In general, the layers, from the steel base outward, comprise a thick layer of wustite, which composition approximates the formula FeO, a layer of magnetite (Fe₂O₃) and a thin layer of hematite (Fe₃O₄) (Turgoose and Bullough, 2013). The husk tends to protect the metal from further oxidation at high temperature.

However, in practice, the oxide layer breaks, increasing the thickness of the film, which tends to peel, increasing at the rate of oxidation. High temperatures and high heating rates cause cracking and breakage in the oxide film sheets, although this can also occur at relatively low temperatures. Rapid temperature fluctuations can also lead to the breakage of the protective oxide layers (Fig. 1).

The removal of the husk to apply a subsequent coating is carried out by pickling the steel in a solution of sulfuric or hydrochloric acid, then washing the steel with water to drag the remains of acid and dissolved iron. These waters are usually taken to a physicochemical treatment station to remove the remains of acid and iron. The surface oxides pass to the solution in the form of sulfate or chloride, depending on the stripper, integrating the residual pickling liquors.

In the pickling process when carbon steel is immersed in acid, this acid penetrates through the cracks and pores of the upper layers of the scale and quickly attacks the wustite layer, thus releasing the relatively insoluble layers of magnetite and hematite.

Iron dissolves to form ferrous ions, and magnetite is reduced, forming more ferrous ions. Since all three compounds are good electrical conductors, the resistance is so small that the dissolution rate of the wustite layer depends on the rate at which the acid diffuses through the cracks into it, and the rate at which the spent acid diffuses from it. A similar but slower action occurs between the exposed metal and the layers of magnetite and hematite that have not come off (Turgoose and Bullough, 2013).

Pickling waters from steel industry are listed as hazardous wastes by the EU Waste Framework (Directive UE 2018/851, 2018) and most of the industrialized countries. Pickling waters corrosive nature is considered an important environmental problem. Many solutions have been used to avoid disposal; however, they are not always adequate or economically viable.

The objective of this work is to carry out a bibliographic review of the existing scientific literature on steel pickling, focusing mainly on those processes that are developed on an industrial scale.
2. CARBON STEEL PICKLING WITH CHLORIC ACID

Numerous methods have been used to remove iron oxides from metal surfaces. These methods include abrasive jet cleaning, tubes, brushing, acid pickling, salt bath decalciﬁcation, alkaline decalciﬁcation, and acid cleaning. The preferred method in steel production is pickling in acid. A solution of hydrochloric acid (HCl) or sulfuric acid (H_2SO_4) is usually used to remove the rust of carbon steel, while for stainless steel a combination of hydroﬂuoric and nitric acids is often used. Among all acids, hydrochloric acid is preferentially used commercially. Beginning in 1964, numerous steel pickling facilities switched from sulfuric acid to hydrochloric acid. Hydrochloric acid offers the following advantages over sulfuric acid and other acids (Hudson and Warning, 1982)
- It provides shiny and smooth surfaces.
- It carries a lower possibility of localized corrosion than with other acids.
- Ferrous chloride salts do not act as process inhibitors until high concentrations.
- It washes easily due to the high solubility of chlorides.
- Galvanic coatings adhere better to metal, more easily and are more uniform.
- Less energy is consumed because the required temperature is lower.

In addition, hydrochloric acid compared to other acids that have been used, for example, nitric acid and phosphoric acid, is safer for the environment, since it does not release effluents containing nitrogen and phosphorus (Agrawal and Sahu, 2009) which can cause eutrophication problems in freshwater bodies.

The main drawbacks of pickling with HCl are the cost, higher than that of H_2SO_4, and the need to install steam control systems. (Hudson and Warning, 1969).

Acid pickling with HCl is a chemical process for dissolving iron oxides from the metal surface without any signiﬁcant attack on the steel itself. The need of the steel industry to provide a high quality of its products is evident, that is why they require a complete removal of rust on the surface that cannot tolerate insufﬁcient pickling, nor too long a permanence of steel products in the pickling operation (Staley, 1926b; Yang et al., 2020).

Due to these reactions, the oxidized layer detaches from the surface, which constitutes an important action in the pickling operation (Staley, 1926b; Yang et al., 2020). Although most of the hydrogen produced in the cathodic areas is released as a gas and helps to remove scale by reducing Fe^{3+} to Fe^{2+} within the solution, some of it diffuses into the steel in atomic form and can make it brittle (weakening of steel by the hydrogen action).

Hydrogen in solution, as stated above, can act as a reducer to dissolve and reduce Fe_3O_4 into FeO in the pickling solution (Özdemir et al., 2006). However, the hydrogen formed adsorbed on the base surface can penetrate the metal layer, which can weaken the binding forces of the layer and reduce the deformation capacity of the metal (Paatsch, 2011; Yang et al., 2020). Due to the reduced ductility, brittle fracture of metallic materials occurs when an external tensile load is applied. (Kuron, 1986; Treischel, 1919; Yang et al., 2020) this process is commonly known as hydrogen embrittlement.

One of the solutions to deal with this problem is the addition of inhibitors in the pickling solution. Inhibitors are speciﬁcally adsorbed in places where the base steel is exposed to form thin layers that prevent the attack of the metal by acid (Feser et al., 2002; Yang et al., 2020). Another practical method is to reduce the immersion time of the metal in the pickling solution and thus reduce the absorption of hydrogen (Staley, 1926a; Yang et al., 2020).

2.1. Acid volatility

The main drawback of using hydrochloric acid is its high volatility under pickling conditions. Gaseous hydrochloric acid causes corrosion to the equipment during and after the pickling process and increases the consumption of pickling solution (Sittig, 1981; Evans et al., 2011; Yang et al., 2020). In addition, HCl gas emissions, if not contained, can cause acidification of the surrounding land.

The temperature favors the pickling process. Pickling efﬁciency can be roughly doubled with an increase of 10 °C (Garverick, 1994; Yang et al., 2020). However, the volatilization of hydrochloric acid is accelerated with the increase in temperature due to the endothermic nature of the volatilization process and the loss of HCl in the bath decreases the efﬁciency of the layer. In addition, as the concentration of HCl in the solution increases, evaporation increases (Yang et al., 2020).

The existence of ferrous ions in the hydrochloric acid solution can effectively inhibit the volatilization of hydrochloric acid (Yang et al., 2020).

2.2. Acid Inhibitors

During the pickling of carbon steel, the ﬁner and more soluble scale is removed before the thicker and

\[
\begin{align*}
\text{Fe}_2\text{O}_3 + \text{Fe} + 6\text{HCl} & \rightarrow 3 \text{FeCl}_2 + 3\text{H}_2\text{O} \\
\text{Fe}_3\text{O}_4 + \text{Fe} + 8\text{HCl} & \rightarrow 4 \text{FeCl}_2 + 4\text{H}_2\text{O} \\
\text{FeO} + 2\text{HCl} & \rightarrow \text{FeCl}_2 + \text{H}_2\text{O}
\end{align*}
\]
less soluble scale. Consequently, part of the exposed base metal is attacked before the pickling operation is completed. To minimize this acid attack, acid inhibitors are used. Its use also causes a lower consumption of acid, fewer marks appear on the surface of the pickled steel and the amount of acid aerosols and water vapor is reduced. In addition, pickling blister formations due to the existence of occluded hydrogen under the surface of the metal, roughness and pitting caused by excessive dissolution of the metal are reduced.

The addition of corrosion inhibitors in the acidic medium is the cheapest and most convenient. Although inhibitors reduce the attack of acids, they do not prevent the attack of oxidizing agents on the exposed base metal. Thus, the ferric ions resulting from the gradual dissolution of the detached magnetite and hematite attack the exposed steel even in the presence of an inhibitor, after this attack these ferric ions become ferrous.

Many acid-soluble or colloidal dispersive organic substances have been shown to have inhibitory properties. The reaction mechanisms of the inhibitor on the metal are complex. Mechanisms of organic-metal composite reaction based on electrostatic attraction between molecules and the charged metal have been described (Ostovari et al., 2009) interaction of uncharged electron pairs of the organic molecule with the metal (Ostovari et al., 2009) interaction of n-electrons with the metal (Ostovari et al., 2009) and finally, combination of those of the first and third (Ostovari et al., 2009).

3. RECYCLING AND REUSE OF SPENT ACID

The corrosive nature and high concentration of acids and metals result in decay acid being considered special hazardous waste (Dahlgren, 2010; Directive UE 2018/851, 2018). In addition to the corrosivity, the main effects of this wastewater on the receiving medium are as follows:

- Hydrolysis of ferrous salts to ferrous-ferric hydroxides, insoluble in water, give rise to an ochre-coloured sediment.
- Iron reduces dissolved oxygen in water, which decreases the regenerative power of rivers.
- Proliferation of ferruginous bacteria, together with the ferritic deposits affect the flora and fauna.
- Concentrations of dissolved iron in water disqualifies its use for food, domestic and industrial purposes.

Increasingly stringent regulations on the discharge of acids and metals into the environment, and the increasing emphasis on the recycling or reuse of these effluents after treatment, have focused the interest of the research community in the development of new approaches to the recovery of acids and metals from industrial waste. The regeneration of acids from pickling allows for several benefits: the reduction of hazardous gas emissions, increased pickling productivity, greater environmental responsibility and promoting the principles of best available technology (BAT) (Regel-Rosoeoka, 2010; Tang et al., 2016).

3.1. Pickling processes with HCl and resulting waste

3.1.1. Continuous pickling process

The continuous pickling process is used to treat coils, rods, wires, and tubes, in the sense that the steel is connected from end to end and continuously passes through the pickling tanks (Fig. 2). The pickling of coils is done by joining the different bands by means of a welding machine, even a stapling machine or a much more basic system, coil to coil processing, also known as “push-pull”. The latter makes productions smaller due to its low productivity. After the continued pickling process there is usually a water cascade wash to clean the surface of traces of solution. This wastewater is sent along with the effluent from the scrubber to a physicochemical treatment plant to neutralize the acidity and precipitate the metals. Finally, the steel is dried before passing it to the next process either oiled, galvanized, painted.

3.1.2. Batch pickling process

The batch process is used to descale rods or wires into coils, pipes, and metal parts. The material is immersed in the pickling tank for a certain period until the scale dissolves (Fig. 3). Each pickling process is followed by a rinsing stage to remove the remains of solution from the metal surface, which in turn is treated in a physicochemical treatment plant like that is used for the washing waters of the continuous pickling process. This process is mainly used as a pre-treatment in the galvanizing process of already formed steel products. Initially these products are degreased to remove traces of oils and oil emulsions. Once the organic impurities are removed, the steel is pickled to remove the oxides from the surface. Finally, just before galvanizing, they are immersed in a chemical flux composed of a double salt of zinc chloride and ammonium chloride, which is designed to chemically remove the last traces of oxides and produce an intense cleaning of the metal surface. These salts favor the wetness of the steel surface by molten zinc, improving the iron-zinc alloy reaction.

In addition to the pickling solution, this process generates numerous wastes such as sludge, which originates in wastewater treatment and flux regeneration plants that are sent to landfill as hazardous waste, zinc ash and dross that can be recycled into metallic zinc and zinc oxide and finally galvanizing powders that are collected in filter sleeves and also sent to landfill as hazardous waste.

The residue resulting from pickling with hydrochloric acid, both in continuous and batch processes, is an acidic solution of ferrous chloride that is classified as hazardous waste (Directive UE 2018/851, 2018) main-
ly because of its high corrosivity, but also because it can be classified as hazardous due to its metal content. There are mainly two types of solutions that correspond to the types of pickling processes already mentioned:

Continuous pickling process liquor: the continuous pickling process is done in closed tanks and at temperatures between 50-80 °C. This means that the main content of the spent acid is a mixture of FeCl₂ in solution, together with the HCl that has not reacted with the scale.

Batch pickling process liquor: The pickling of carbon steel parts is done in open tanks and at room temper-
perature and constitutes a process prior to galvanizing. In this case, the liquors are known as galvanic pickling liqueurs and not only contain ferrous ions, but also other metal ions such as Zinc. Zinc contamination enters the pickling line through hooks, insoles, cages, and baskets that are used to suspend batches of carbon steel parts during immersion. These are galvanized, sent back to the head of the plant for reuse, and stripped during pickling of the next workpiece, thus contaminating the galvanic pickling liquor with zinc. This liquor is, therefore, a solution containing various concentrations of HCl, and salts in solution of FeCl$_2$ and ZnCl$_2$.

3.2. Technological solutions to reuse or recycle used pickling solutions with HCl

There are many studies aimed at the recovery of value contents in pickling waters. These studies are based on two principles the recovery of the existing free acid waters and metals recovery.

3.2.1. Ferric chloride production

The most used method to obtain ferric chloride is based on the use of pickling liquors. It is a more cost-effective method than dissolving ferrous scrap in hydrochloric acid.

The first step in the production of ferric chloride from pickling waters is the removal of free acid by adding scrap. After this reaction, the resulting solution without free acid is chlorinated with chlorine gas to form ferric chloride through reaction (5) (Inguru Consultores, 2006):

$$2\text{FeCl}_2 + \text{Cl}_2 \rightarrow 2\text{FeCl}_3 \quad (5)$$

Once the solution reaches 40% concentration of FeCl$_3$, the process is concluded and ready to be marketed in the form of a solution. The most common end use is coagulant of contaminants in wastewater treatment.

3.2.2. Recovery of free hydrochloric acid and other by-products for pickling operations

Various technologies have been proposed to recover free acid. HCl is a volatile compound and the liquid-vapor balance is influenced both by temperature and by the concentration of acid and ferrous salts in the solution (Tomaszewksa et al., 2001) which means that its recovery requires technologies that can involve a high investment cost. The most outstanding technologies are:

a) Acid Retardation or Ion Exchange Resins is a process in which metal ions are separated from acids by their mobility difference. The spent pickling solution passes through an anionic-type ion exchange resin that favors the absorption of strong acids. The movement of acids in the ion exchange resin is delayed relative to the movement of salt and water flowing faster (Hatch and Dillon, 1963; Bood, 2020). The acid is desorbed from the ion exchange resin by backwashing with water. Due to its simplicity, reliability, and relatively low cost, acid retardation is one of the most common purification techniques for spent pickling solutions (Naushad and Al-Othman, 2013; Bood, 2020). The main disadvantage is the iron scales or some other impurities that can be produced in resins. On the other hand, this type of membranes only absorbs a part of the acid, so the problem is only partially reduced (Palatý and Žáková, 2006).

b) Diffusion dialysis (DD) is a membrane process that operates under some of the same principles as ion exchange resins (acid delay) using ion-selective membrane material. Clean water (dialyzed) is introduced countercurrent into the permeate side of the membrane to absorb the acid passing through the semipermeable surface. Diffusion dialysis is an ongoing process. Compared to other membrane technologies (e.g. electrodialysis or reverse osmosis), in addition, the diffusion dialysis process does not work with electrical potential or pressure difference across the membrane. For the pickling system with HCl, iron chlorides were found to provide additional chlorides in solution that improve acid passage (Luo et al., 2013; Gueccia et al., 2019; Gueccia et al., 2020; Gueccia et al., 2021) In contrast, zinc ions in acid solution are mainly present as negative chlorine complexes, which act as competitors to acid recovery, thus reducing the passage of acid (Jung et al., 2000).

c) Pyro-hydrolysis is a roasting process in which acidic ferrous chloride is burned to produce iron oxide and gaseous hydrogen chloride. It is used as an effective way to fix iron as an oxide, for sale as a by-product or for safe disposal and to produce hydrogen chloride gas that reacts with incoming water (usually washing water from the pickling process) to form almost azeotropic hydrochloric acid. There are mainly two technologies available: fluidized bed and spray roasting (Lee et al., 2006). The main drawback of pyrohydrolysis is that it consumes a lot of energy (Stocks et al., 2005; Devi et al., 2014; Gueccia et al., 2021) and suffers from the presence of zinc in solution, due to the formation of low melting compounds at the high working temperature of the process (Kerney, 1994). This technology was widely used in past but the drop in the price of HCl and the high energy cost made it unattractive. In spray roasting units, the exhaust gases and oxides leave the roaster in counter current flow at temperatures in the range of 400 °C to 500 °C. Due to the counter current flow, the exit temperature in the spray roaster is lower than the temperature of the reaction zone. The residence time of the sprayed particles in the high-temperature reaction zone is very short; therefore, very small liquid droplets

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must be created by atomisation, which can be heated quickly. Rapid heating results in the formation of a solid metal oxide crust on the surface of each droplet. As the bulk of the droplet is heated, the water content vaporises and breaks through the oxide layer. Therefore, spray-roasted oxides often consist of very fine hollow spheres.

In fluidised beds, the gas and solids are completely mixed, and their outlet temperature is normally 800 °C to 900 °C, which is the same as that of the reaction zone. The hot flue gas is normally produced by submerged nozzles that directly inject air and fuel into the bottom of the fluidised bed. The hot gas flows upwards and fluidises the particulate bed. As the flue gas flows through the well-stirred oxide bed, it quickly reaches thermal equilibrium with the bed. The liquid dosage of solution is not sprayed but poured directly into the oxide bed. The solution wets the outer layer of the hot oxide particles and quickly evaporates to form a layer of new solid oxide on top of the existing oxide, thus producing dense homogeneous particles.

d) Evaporative recovery by which the solution of HCl, water and metal salt enters a vacuum evaporator and is heated above the boiling point of the HCl (108.6 °C) (Cullivan, 2020). To keep the heat sensitive and ensure a more efficient heat cycle, the forced circulation of the spent pickling solution generates a slight back pressure. With the rest of the process operating under vacuum, the pressurized and heated solution is sprayed into a separator where both water and hydrochloric acid evaporate simultaneously (Cullivan, 2020). The remaining metal chloride salt solution is concentrated as more spent acid enters the evaporator and the HCl/H₂O solution vaporizes (Cullivan, 2020). When the specific gravity of the metal salt reaches the target, the metal chloride concentrate is pumped into a storage tank for transport to an end user. HCl/H₂O vapor travels through a rectifier filled with an acid-resistant material, where the water descends from the top and mixes with the HCl vapor as it descends. Condensed steam droplets increase their acid concentration as they descend and approach the azetotropic point of HCl at 20%. The remaining water vapor goes through the filter, into a water-cooled condenser. The steam condenses into reusable process water.

To be more efficient, evaporative recovery works under partial vacuum. This reduces the boiling point of HCl from 108.6 °C to less than 80 °C. Vacuum processing reduces energy consumption, construction cost and the potential for chemical excursions (Cullivan, 2020).

3.2.3. Selective metal recovery technologies

The water treatment industry uses large amounts of ferric chloride as a flocculant in treated wastewater treatment before discharge into surface water. Ferric chlorides do not occur naturally and must be manufactured as indicated in section 3.1 from spent pickling solutions. However, in order to reuse this pickling solution it is always necessary that the iron chloride is at a high level (>130 g·l⁻¹ of Fe) and the zinc chloride is below a specified level (<1 g·l⁻¹ of Zn) (Stocks et al., 2005).

There are several chemical separation techniques that could achieve the separation of iron and zinc from these acid wastes, such as chemical precipitation, ion exchange and solvent extraction, but also includes crystallization that, although it is not valid for the separation of metals if it is to recover metals in the form of salts.

a) Chemical precipitation: consists of the removal of iron in the form of Hydroxides Fe(OH)₃. However, in galvanic pickling waters, no chemical can be found that selectively precipitates Zn from solutions high in Fe²⁺ without contaminating the precipitate with Fe and leaving the residual Zn dissolved (Kerney, 1994). This technique is usually carried out after having recovered or spent almost all the hydrochloric acid from the pickling solution, since the following steps require oxidizing FeCl₂ to FeCl₃ and then precipitating the iron increasing the pH of the solution. If the pickling solution contains ZnCl₂ in addition to FeCl₃, the increase in pH is made with the addition of ammonium hydroxide. Zinc ions remain in solution along with ammonium chlorides, due to their higher precipitation pH values (Gueccia et al., 2019; Gueccia et al., 2021). Once the iron is removed, the resulting solution would form a double salt of NH₄Cl and ZnCl₂, very similar to that used as a flux in the galvanizing process, although it should be adjusted to be reused. The precipitate of iron hydroxides is difficult to market, so its destination will most likely be the landfill.

b) Separation of ion exchange resins: it is an effective procedure for removing metals present in industrial effluents (Bolton and Pawlowski, 1987; Meltzer, 1990; Marañón et al., 2000), since dissolved metal ions are retained in the resin bed by a reversible reaction. When this bed becomes saturated, it must regenerate, passing the ions to the regenerated solution. The regenerated volume is much smaller than the volume of treated effluent, so the metals are in a much higher concentration in the regenerated liquid and can be properly treated by precipitation, distillation or other recovery processes (Marañón et al., 2000). The affinity of zinc for resins allows iron to be removed in the presence of zinc in the solution (Marañón et al., 2000). However, it is also necessary to initially oxidize Fe²⁺ to Fe³⁺ which then forms an anionic complex that helps not to interfere with zinc (Marañón et al., 2000).

The use of ion exchange resins for metal separation only works with low concentrations of iron and
zinc (Marañón et al., 2000). Therefore, a large volume of resin, with high investment costs, would be required to treat the currently generated spent acid, with its high and unpredictable levels of zinc.

c) Extraction with organic solvents (liquid/liquid separation): it is the most consolidated separation technology for the recycling of waste that needs to separate metals. Solvents are becoming increasingly selective, allowing specific molecules to be separated from the aqueous phase while others are preserved. Kerney, 1994 and Agrawal et al. (2011) demonstrated that solvent extraction was a viable treatment process for separating FeCl₂ and ZnCl₂ from HCl.

For the recovery of Zn (II), Fe (II), Fe (III) and HCl from spent pickling solution, various extraction agents such as D2EHPA, DBBP, TBP, Cyanex 921, Cyanex 923, Cyanex 301, Cyanex 302, Cyanex 272, Alamine 336, Alamine 308, Alquat 363, TEHA and TiOA have been applied exhaustively (Kerney, 1994). The above agents simultaneously extract Zn(II) and Fe(III) from the pickling solution. The Zn (II) and Fe (III) present in the organic phase are subsequently separated in the re-extraction stage (Sinha et al., 2016) The re-extraction of the metals extracted in the organic phase is conventionally carried out with acid/base reagents, recovering through precipitation, crystallization or electrodeposition. Of particular interest is the use of Cyanex 923 as an extraction agent for the selective recovery of Zn(II) and Fe(III) (Saji John et al., 1999; Alguacil and Martinez, 2001; Regel et al., 2001; Agrawal and Sahu, 2010; Mishra et al., 2010; Sinha et al., 2016; Regel-Rosocka et al., 2002). In addition, Cyanex 923 is a stable reagent under highly acidic conditions.

d) Crystallization: the recovery of residual pickling acids can also be achieved by crystallization, since the lower the temperature, the lower the solubility of ferrous chloride in the recovered acid stream due to the inverse relationship of ferrous chloride solubility to temperature (Özdemir et al., 2006). Some processes have been developed on the regeneration of spent pickling liquids, including the recovery of acids and metals (Agrawal and Sahu, 2009; Regel-Rosocka, 2010) and new process options based on crystallization have been proposed as alternative methods (Özdemir et al., 2006; Al-Othman and Demopoulos, 2009; Leonzio, 2016) while separation techniques, such as evaporation (Anand et al., 2008) seem to be more appropriate for treating pickling liquids when the metal composition is quite complex. Although when the metal composition is homogeneous, without the presence of zinc, the recovery of acid by evaporation and the crystallization of FeCl₂·4H₂O can be combined upon reaching the saturation point of salt as indicated by the Kleigarn curve (Kleigarn, 1990).

The DECAPVALUE project carried out at the National Center for Metallurgical Research of the Higher Council for Metallurgical Research (CENIM-CSIC) funded by HIASA Contract ID 20200543, has obtained ferrous chloride crystals with FeCl₂·4H₂O in a pilot evaporation-crystallization plant using the company’s pickling liquor. HIASA (Asturias, Spain). Thus, all the results obtained reveal that it is possible to obtain crystals of FeCl₂·4H₂O of high purity and high stability from pickling liqueurs (Alcaraz et al., 2021). The crystallization technique is standard for the regeneration of pickling solutions with sulfuric acid, since at low temperature ferrous sulfate crystallizes very easily. Another alternative offered by crystallization is to add sulfuric acid to the spent pickling solution. Sulfuric acid reacts with ferrous chloride, thus releasing free hydrochloric acid into the solution together with ferrous sulfates according to the reaction (6):

\[
\text{FeCl}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{HCl} + \text{FeSO}_4
\]

The mixed acid is cooled below the freezing point of the water, which causes the crystallization of the ferrous sulfate heptahydrate (Brown, 2006). The pickling solution is now enriched with hydrochloric acid, although it contains traces of sulfuric acid, then separated from the ferrous sulfate crystals heptahydrate that can be easily marketed and the acid reused (Brown, 2006).

4. CONCLUSIONS

The technologies with greater maturity used for the recycling of carbon steel pickling liquors correspond to pyrolysis (fluidized bed and spray roasting), in addition to those oriented to the production of FeCl₂. However, none of these technologies are valid for galvanic liquids and these must be treated with other less mature technologies. In this case, ion exchange resins or solvent extraction must be chosen, but in both cases the metal concentrations and the limitations of each technology must be considered.

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