

Effective recovery of HCl and metals from pickling solutions by cutting-edge membrane technologies

R. Gueccia, S. Randazzo*, A. Culcasi, A. Cipollina, G. Micale

Dipartimento di Ingegneria Chimica, Gestionale, Informatica, Meccanica, Università di Palermo – Viale delle Scienze ed.6, 90128 Palermo, Italy

**Corresponding Author. E-mail: serena.randazzo@unipa.it*

INTRODUCTION

The pickling process is an essential step in the hot-dip galvanizing process. It is performed by immersing manufactured steel pieces in acid baths in order to dissolve the oxidized layers. During the pickling process, acid attacks metal oxides on the surface, dissolving them in the pickling bath. Thus, the efficiency of the pickling liquor decreases due to the accumulation of metal salts and the consumption of free acid in the solution. When hydrochloric acid is used, ferrous chloride is produced during the pickling treatment, reaching concentrations up to 250 g/l, while the acid concentration decreases by 75-85%. A pickling bath in this condition is considered spent [1] due to the very low pickling rate, hence it needs to be replaced. In common industrial practice, part of the exhausted solution is withdrawn and replaced with fresh acid or with a more concentrate solution to prolong the pickling bath life, while spent solution is disposed as a waste.

Disposal of the spent pickling solution strongly affects the hot-dip galvanizing industries footprint and costs, thus the recovery of acid is one of the most beneficial steps to reduce the environmental and economic impact. In particular, continuous regeneration of pickling solutions can enhance pickling rate and process performance, but also reduce industrial wastewater disposal and chemicals consumption. The recovery and recycling of valuable compounds (e.g. acid, metals and water) can be accomplished by coupling two cutting-edge membrane technologies: diffusion dialysis (DD) and membrane distillation (MD) [2,3]. Membrane techniques are considered simple, effective and sustainable [1] and can be easily scaled from small to medium size installations.

In the present work, a case study is presented, relevant to the hot-dip galvanizing plant of TecnoZinco (Palermo, Italy). The site has a capacity of 20,000 tons per year of treated steel. Starting from an accurate data mining, a Process Flow Diagram (PFD) of an integrated process that provides a continuous regeneration of pickling solution is proposed, within the framework of the EU-funded ReWaCEM project (www.rewacem.eu), with the final aim of building a pilot plant to be installed and operated in real environment.

A steady state process simulator for the integrated process has been developed, aiming to design, analyze and predict performance of the pilot unit. A parametric analysis of the model is performed varying hydrochloric acid in the stream going out from the pickling tank. Results presents the perspective operation of such plant, indicating the technical feasibility of the novel developed process.

HOT-DIP GALVANIZING PROCESS AT TECNOZINCO PLANT– MAIN ASPECTS

Hot-dip galvanizing process includes several steps. Following the pathway shown in Fig. 1, the manufactured steel is first degreased in a bath under action of surfactants, then is transferred in a pickling tank, washed in a rinsing tank and put in a fluxing bath before drying and galvanizing. The fluxing solution contains zinc chloride to protect the manufactured steel before the immersion in the molten zinc bath and ammonium chloride to catalyze zinc covering.

Pickling process is performed by immersing manufactured steel in hydrochloric acid (HCl) bath. The acid dissolves the oxidized layers of the manufactured steel leading to the formation of iron(II) chloride in the pickling solution. The kinetic of these reactions is strongly affected by the presence of the acid molecules and also by the iron ions concentration. A specific relationship between the acid and the iron concentration for optimal pickling operation is reported in the literature as the *Kleingarn Curve* (Fig. 2). As a consequence, controlling acid and iron concentrations within the tank increases pickling rate compared to replacing the entire spent acid bath with fresh acid. Note that, the composition of some samples from Tecnozinco pickling baths is reported as an example in the graph (Fig. 2).

Tecnozinco facility uses 7 pickling bathes containing in total more than 350 m³ of acid pickling solution. The acid consumption is approximately 160-240 ton per year. Bathes can be grouped in three classes according to the “pickling power”, i.e. highly effective pickling (HCl 120-160 g/L, Fe 50-80 g/L - area A in Fig. 2), intermediate effective pickling (HCl 80-120 g/L, Fe 80-150 g/L - area B in Fig. 2) and poorly effective pickling (HCl 20-80 g/L, Fe 150-180 g/L - area C in Fig. 2). Based on periodical analysis of free acidity and iron content, HCl and Fe concentrations are varied to reach the optimal

pickling rate by spilling part of the solution and subsequent replenishing.

Besides iron ions, also zinc is present in the pickling tanks of hot-dip galvanizing plants where goods and winches used for pieces handling are often covered of zinc. Therefore, the pickling process generates a waste acid stream of approximately 300 ton per year, characterized by high concentrations of heavy metals, namely iron (150-180 g/L) and zinc (10-30 g/L). Disposal costs incurred by Tecnozinco include transportation to a far waste treatment plant in northern Italy.

INTEGRATED PROCESS DESCRIPTION

The proposed integrated process aims at synergically merging DD and MD processes to keep HCl and iron concentrations in the pickling tank at the optimum concentrations. The Process Flow Diagram is shown in Figure 3. Starting from the pickling tank, the outgoing stream, named *Waste Acid solution (WAS)*, after a pre-treatment, is sent to the Diffusion Dialysis unit (in the retentate side) in which the recovery of the acid occurs. Here, the acid stream is separated from the metal ions due to the anionic exchange membrane. In fact, due to the positive charge of the membrane, the transport of chlorides is permitted. However, also H⁺ ions can diffuse through the anionic membrane, despite own positive charge, for their little dimension and do to the tunneling mechanism [3,4]. Conversely, other positive charged ions, iron and zinc cations for instance, are rejected because of the electrostatic repulsion. Therefore, the acid is recovered in the diffusate side of the DD unit and separation from salts occurs. Nevertheless, as reported in literature and as observed in our research investigation campaign, iron and zinc can pass through the membrane, reaching leakage percentage of 5-10% for iron and up to 50-60% for zinc [4].

The stream enriched in acid, named *Recovered Acid Solution (RAS)* is sent to the MD unit, where the acid is concentrated. Membrane Distillation achieves the concentration of acid due to water evaporation. In fact, it is a process in which a microporous hydrophobic membrane separates two aqueous solutions at different temperature and composition. The driving force for MD is the partial pressure difference induced by the temperature and composition of the layers adjacent to the membrane [2]. This specific membrane rejects water and permits steam passage, thus water can be recovered once the steam condenses directly in the solution (*Permeate* stream) in the cold compartment. In MD, also some HCl is transported through the membrane [2]. The *Permeate* stream from MD is sent to the DD unit (in the diffusate side), after the addition of a *Process Water (PW)* stream,

necessary to reach the desired flow rates inside DD unit. This stream is named *Draw Solution (DS)*. The stream outing from MD concentrated in acid, the *Recovered Pickling Solution (RPS)*, is sent to the pickling tank.

The other stream coming out from the DD unit in the retentate side, called *Metals Rich Brine (MRB)*, is an acid stream enriched in iron and zinc chlorides. In order to compensate the acid lost here and the acid reacted in the pickling process, a *Make-Up (MU)* of fresh acid is added in the pickling bath.

Even the metals are recovered in the proposed integrated process. In fact, the *Metals Rich Brine (MRB)* stream is sent to a Reactive Precipitation unit in which the acid is neutralized and, at the same time, the iron is recovered as hydroxide by precipitation with ammonia. The addition of hydrogen peroxide in the reactive precipitation process is needed to oxidize Fe²⁺ to Fe³⁺.

The stream generated from this step, after separation of solids by filtration, is sent to a Brine Membrane Distillation unit. Here, distillate water and a more concentrated ammonium and zinc chloride solution are produced which can be used, the first as process water, the latter in the fluxing bath of the pickling plant.

As previously mentioned, the pilot-scale unit will be installed at Tecnozinco, where also a recovery of waste heat (necessary for the MD operation) is foreseen for enhancing the process sustainability.

MODELING OF THE INTEGRATED PROCESS

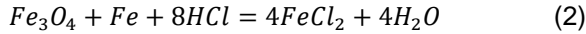
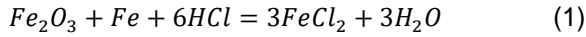
A mathematical model able to design and predict the integrated system operations was developed and implemented in an Excel spread sheet with Macros in Visual Basic language.

Data Mining

The first step of the modelling activity was to fix parameters and operative conditions of the pickling process. Looking at Figure 3, the streams took into account to start the modelling activity were the inlets of manufactured steel, acid make-up, entrainment from the previous step of degreasing and the outlets of entrainment, water evaporation and HCl gas emission. The main important information was the consumption of the acid per ton of steel manufacturing. In order to estimate this value, two possible options were possible: using kinetics data from literature or collecting information from historical statistics of the company. In this work, the latter was selected as starting point. Moreover, fixing a time frame of 1 year, real data from Tecnozinco have been collected regarding the bath pickling volume, the quantity of manufacturing steel, acid make-up, the starting bath composition and the quantity of exhausted solution disposed. Other data, such as inlet and outlet entrainment volumetric flow rates

were derived from work experience. All these information allowed the closure of the pickling overall mass balance, estimating the water evaporation rate.

The calculations were figured out by considering Eq. (1-2) as the main chemical pickling reactions when corrosion inhibitors are used [5]:



It was assumed that the reaction (1) accounts for the 20% and the reaction (2) for the 80% of the acid consumption according to the scale composition [6]. Thereafter, conversion rates of species involved in the pickling process were calculated by adopting the following expression:

$$w_i = k_i \cdot w_s \quad (3)$$

where w_i and w_s are mass flow rates [ton/h] of the i -component and of the manufactured steel, respectively, and k_i is the kinetic constant of the i -component. k_i values were evaluated under the assumption of a complete stoichiometric conversion of the reagents.

Model assumptions

In order to develop the mathematical model the following hypotheses were assumed:

1. The process is modelled in steady state conditions;
2. The amount of steel manufactured is fixed;
3. The pickling bath and the reactive precipitator are considered as a CSTR reactors;
4. The ratio between the DD inlet volumetric flow rates is fixed to 1;
5. The minimum ΔC driving force between HCl concentrations of the retentate and diffusate streams in the DD unit is fixed at 3 g/L;
6. The pH of the outlet stream of the reactive precipitator is fixed at 4;
7. The Metals Sludge exiting the precipitation reactor contains 35% of the total solution outgoing from the reactive precipitator.

Pickling tank

The streams related to the pickling tank are: *Waste Acid Solution*, *Acid Make-Up*, *Process Water* (Fig. 3).

The pickling batch is modelled as a continuous perfectly-mixed reactor. As a result, the volumetric flow rate coming from the pickling bath is calculated by the Equation 4.

$$F_{WAS} = \frac{k_{Fe} \cdot w_s + w_{Fe}^{DD} + w_{Fe}^{entr,in}}{C_{Fe}} \quad (4)$$

where F_{WAS} is the *Waste Acid Solution* volumetric flow rate [lt/h], k_{Fe} is the iron production constant, w_s is the manufactured steel mass flow rate [ton/h], w_{Fe}^{DD} is the iron mass flow rate [kg/h] recovered by the Diffusion dialysis process and $w_{Fe}^{entr,in}$ is the iron flow rate inlet in the pickling bath with the entrainment stream from the rinsing tank [kg/h]. C_{Fe} represents the optimal iron concentration on the basis of the linear regression of the so-called Kleingarn Curve (see Fig. 2), reported in Eq. 5:

$$C_{Fe} = -0,8333 \cdot C_{HCl} + 200 \quad (5)$$

To evaluate the process streams mass density, the model developed by M. Laliberté et al. was adopted [7]. As a consequence of the assumptions 1 and 3, the *Waste Acid Solution* composition is constant during the process and it is equal to the composition inside the pickling tank.

The mass flow rate of the acid *Make-Up* stream is calculated by the following equation

$$w_{HCl}^{MU} = w_{HCl}^{MRB} + k_{HCl} \cdot w_s + w_{HCl}^{entr,out} \quad (6)$$

where w_{HCl}^{MU} , w_{HCl}^{MRB} and $w_{HCl}^{entr,out}$ are the hydrochloric acid mass flow rate [kg/h] of the *Make-Up*, *Metals Rich Brine* and *Entrainment,out* streams, respectively. $k_{HCl} \cdot w_s$ term concerns the HCl flow rate reacted in the pickling process [kg/h]. The *Make-Up* stream is necessary within the pickling bath to compensate the hydrochloric acid outlet from the diffusion dialysis unit in the *Metals Rich Brine* stream. The *Entrainment,out* stream is dragged by the transfer of the manufacturing steel from the pickling tank to the rinsing tank.

The *Process Water* stream is evaluated by performing a global mass balance using the entire integrated system as computing volume (Eq. 7).

$$w_{tot}^{pw} = w_{tot}^{MRB} + w_{entr,out} + w_{evap} - w_{tot}^{MU} - k_{oxides} \cdot w_s - w_{entr,in} \quad (7)$$

where

w_{tot}^{pw} , w_{tot}^{MRB} , $w_{entr,out}$, w_{evap} , w_{tot}^{MU} and $w_{entr,in}$ are the water mass flow rate [kg/h] in the *Process Water* incoming into the system, in the *Metals Rich Brine*, in the *Entrainment,out*, in the evaporation, in the *Make-Up*, and in the *Entrainment,in* streams, respectively. $k_{oxides} \cdot w_s$ term concerns the oxides mass flow rate inlet within the manufactured steel in the pickling tank [kg/h].

Diffusion Dialysis unit

Concerning the Diffusion Dialysis unit, the other streams that have to be characterized for the integrated process design are: *Recovered Acid Solution*, *Draw Solution*, *Metal Rich Brine* (Fig. 3). Main balances used in this section derived from the results obtained from an experimental campaign carried out by some of co-authors [10]. Experiments were performed with a DD laboratory test-rig, where a Fumatech FAD-type Anionic Exchange Membrane (AEM) was adopted, in order to collect information for calibrating/validating the model before using it for design purposes.

The hydrochloric acid recovery was obtained by using Eq. 8.

$$w_{HCl}^{DD} = A \cdot PM_{HCl} [P_{j,HCl} \cdot (C_{HCl,mol}^R - C_{HCl,mol}^D) + U_s \cdot (C_{Fe,mol}^R - C_{Fe,mol}^D)] \quad (8)$$

where w_{HCl}^{DD} is the mass flow rate of hydrochloric acid [kg/h] passing from the retentate to the diffusate side of the DD unit, A is the membrane area [m²], $P_{j,HCl}$ is the membrane permeability to the hydrochloric acid [m/h], U_s is the further permeability to the passage of acid due to the presence of the corresponding anion salt [m/h], $C_{HCl,mol}^R$, $C_{HCl,mol}^D$ and $C_{Fe,mol}^R$, $C_{Fe,mol}^D$ are the average concentrations of hydrochloric acid and iron in the retentate and in diffusate side [mol/l], respectively. The expression for $P_{j,HCl}$ and U_s was derived experimentally [8] and it is reported in Eq. 9 and 10.

$$P_{j,HCl} = 1.16 \cdot 10^{-3} C_{HCl,mol}^R{}^3 - 6.95 \cdot 10^{-3} C_{HCl,mol}^R{}^2 + 1.48 \cdot 10^{-2} C_{HCl,mol}^R + 2.38 \cdot 10^{-3} \quad (9)$$

$$U_s = 1.09 \cdot 10^{-2} C_{HCl,mol}^R + 2.18 \cdot 10^{-3} \quad (10)$$

Despite the anionic exchange membrane rejects in theory all iron ions, a small passage of iron chloride is observed [4,8]. Therefore, salt diffusion through the AEM membrane was considered by using Eq. 11.

$$w_{Fe}^{DD} = A \cdot P_{j,Fe} \cdot PM_{Fe} (C_{Fe,mol}^R - C_{Fe,mol}^D) \quad (11)$$

where w_{Fe}^{DD} is the iron mass flow rate [kg/h] passing from the retentate to the diffusate side of the DD unit, A is the membrane area [m²], $P_{j,Fe}$ is the membrane permeability to the FeCl₂ [m/h], $C_{Fe,mol}^R$ and $C_{Fe,mol}^D$ are the iron average concentrations in the retentate and in the diffusate side [mol/l], respectively. The expression for $P_{j,Fe}$ was derived experimentally [8] and it is reported in Eq. 12.

$$P_{j,Fe} = -6.73 \cdot 10^{-5} C_{Fe,mol}^2 + 4.21 \cdot 10^{-4} C_{Fe,mol} + 1.08 \cdot 10^{-4} \quad (12)$$

in which $C_{Fe,mol}$ is the average iron molar concentration [mol/l] in the retentate side of the DD unit.

Concerning the zinc passage, similar considerations were accomplished by using a leakage percentage of 35% derived from the experimental campaign carried out [8].

Two contributions for the water passage are considered: the osmotic and the drag fluxes through the membrane. The osmotic flux J_{osm} is calculated by Eq. 13.

$$J_{osm} = R \cdot T \cdot P_w \cdot \rho_w \cdot (2 \cdot \Delta C_{HCl,mol}^{av} + 3 \cdot \Delta C_{Fe,mol}^{av} + 3 \cdot \Delta C_{Zn,mol}^{av}) \quad (13)$$

where R is the gas constant [lt bar/(K mol)], T is the average temperature [K], P_w is the water permeability [lt/(m² h bar)], ρ_w is the water density (kg/dm³), $\Delta C_{HCl,mol}^{av}$, $\Delta C_{Fe,mol}^{av}$ and $\Delta C_{Zn,mol}^{av}$ are the average concentration difference [mol/l] in the DD of the HCl, Fe and Zn respectively. The expression for P_w was derived experimentally:

$$P_w = 6.1 \cdot 10^{-3} C_{HCl,mol}^R + 2.2 \cdot 10^{-2} \quad (14)$$

in which $C_{HCl,mol}^R$ is the average hydrochloric acid molar concentration [mol/l] in the retentate side of the DD unit. The drag flux J_{drag} is calculated according to the following equation:

$$J_{drag} = \left(7 \cdot \frac{w_{HCl}^{DD}}{MM_{HCl}} + 18 \cdot \frac{w_{FeCl_2}^{DD}}{MA_{FeCl_2}} + 18 \cdot \frac{w_{ZnCl_2}^{DD}}{MA_{ZnCl_2}} \right) \cdot MM_{H_2O} \quad (15)$$

where w_{HCl}^{DD} , $w_{FeCl_2}^{DD}$ and $w_{ZnCl_2}^{DD}$ are the HCl, FeCl₂ and ZnCl₂ mass flow rates [kg/h] passing through the DD membrane, MM_{HCl} and MM_{H_2O} are the HCl and H₂O mole masses [g/mol] and MA_{Fe} is the iron atomic mass [g/mol].

Finally, the overall mass balance for DD unit is reported in Eq. 16.

$$w_{tot}^{DS} + w_{tot}^{WAS} = w_{tot}^{MRB} + w_{tot}^{RAS} \quad (16)$$

where w_{tot}^{DS} , w_{tot}^{WAS} , w_{tot}^{MRB} and w_{tot}^{RAS} are the total mass flow rates of the *Draw Solution*, *Waste Acid Solution*, *Metals Rich Brine* and *Recovered Acid Solution* streams [kg/h].

Membrane Distillation unit

With regard to Membrane Distillation unit, the streams to be characterized are: *Recovered Pickling Solution*, *Permeate* (see Figure 3).

The fluxes of water and HCl in the vapour phase passed through the membrane are derived from simulations carried out by another research partner within the ReWaCEM consortium. The values of J_i [kg/(h·m²)] used in the model are extrapolated from simulation results. Specifically, J_{water} is 3.0-3.1 kg/(h·m²) and J_{HCl} is 0.06-0.12

kg/(h·m²) for the acid concentrations considered in this work.

The overall mass balance for the Membrane Distillation unit is reported in Eq. (17):

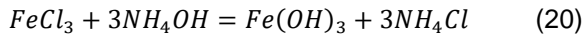
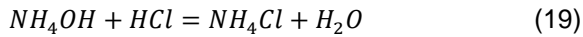
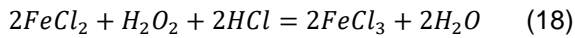
$$w_{tot}^{RAS} = w_{tot}^{RPS} + w_{tot}^{MD} \quad (17)$$

where w_{tot}^{RAS} , w_{tot}^{RPS} and w_{tot}^{MD} are the total mass flow rates of the *Recovered Acid Solution*, *Recovered Pickling Solution* and Membrane Distillation *Permeate* streams [kg/h].

Reactive Precipitation stage

The Reactive Precipitation unit is modelled considering the complete iron precipitation from the solution in the form of iron hydroxide by adding ammonia/water solution (30% w/w). Since the iron in solution is mainly present in the reduced form, especially due to the strong acid conditions, oxidizing is necessary to obtain a high pure iron hydroxide precipitate, free of zinc. In fact, pH precipitation of zinc hydroxide is very similar to iron(II) hydroxide, but higher than iron(III) hydroxide enough to obtain the precipitation of only iron(III) at an operating pH range of 3-4. A 35% of drag solution was considered in the precipitated.

The following reactions are considered in the reactive precipitation process:



The hydrogen peroxide mass flow rate is calculated according to the following expression:

$$w_{H_2O_2}^{Ox} = \frac{w_{Fe}^{MRB} \cdot MM_{H_2O_2}}{2 \cdot MM_{Fe}} \quad (21)$$

where $w_{H_2O_2}^{Ox}$ and w_{Fe}^{MRB} are the mass flow rate [kg/h] of the hydrogen peroxide and iron in the *MRB* stream, $MM_{H_2O_2}$ and MM_{Fe} are the mole mass [g/mol] of H_2O_2 and Fe, respectively.

The mass flow rate of the alkaline reactant is computed using the relation:

$$w_{NH_4OH}^{Alk} = \left[(10^{-pH_{in}} - 10^{-pH_{fin}}) \cdot F_{tot} + 2 \cdot \frac{C_{Fe^{2+}} \cdot F_{tot}}{MM_{Fe}} \right] \cdot MM_{NH_4OH} \quad (22)$$

where $w_{NH_4OH}^{Alk}$ is the reactant mass flow rate [kg/h], pH_{in} and pH_{out} are the initial and final pH of the solution, F_{tot} is the volumetric flow rate [lt/h], $C_{Fe^{2+}}$ is the iron concentration [g/lt], MM_{Fe} and MM_{NH_4OH} are the iron and NH_4OH mole mass [g/mol].

Regarding the *Metals Sludge (MS)* calculations, the following equations are used:

$$w_{H_2O}^{MS} = \left[(10^{pH_{in}} - 10^{pH_{fin}}) \cdot F_{MRB} \cdot MM_{H_2O} + w_{H_2O}^{MRB} + w_{H_2O}^{alk} \right] \cdot \alpha \quad (23)$$

$$w_{HCl}^{MS} = \left[w_{HCl}^{MRB} - (10^{pH_{in}} - 10^{pH_{fin}}) \cdot F_{MRB} \cdot MM_{HCl} \right] \cdot \alpha \quad (24)$$

$$w_{Cl^-}^{MS} = \alpha \cdot w_{Cl^-}^{MRB} + (w_{HCl}^{MRB} - w_{HCl}^{MS} - w_{HCl}^{out}) \cdot \frac{MA_{Cl} \cdot \alpha}{MM_{HCl}} \quad (25)$$

$$w_{NH_4^+}^{MS} = w_{NH_4OH}^{alk} \cdot \alpha \cdot \frac{MA_{NH_4^+}}{MM_{NH_4OH}} \quad (26)$$

$$w_{OH^-}^{MS} = \frac{3 \cdot C_{Fe^{3+}}^{MRB} \cdot F_{MRB} \cdot MM_{OH}}{MA_{Fe}} \quad (27)$$

where $w_{H_2O}^{MS}$, $w_{H_2O}^{MRB}$ and $w_{H_2O}^{alk}$, w_{HCl}^{MS} and w_{HCl}^{MRB} , $w_{Cl^-}^{MS}$, $w_{Cl^-}^{MRB}$ and $w_{Cl^-}^{out}$, $w_{NH_4^+}^{MS}$ and $w_{NH_4OH}^{alk}$, $w_{OH^-}^{MS}$ are the mass flow rates [kg/h] of water, HCl, chloride ions, ammonium cations, ammonium hydroxide and hydroxyl ions in the *Metals Sludge*, *Metals Rich Brine*, Alkaline reactant and out from the reactive precipitator streams respectively, pH_{in} and pH_{fin} are the initial and final pH of the solution, F_{MRB} is the *MRB* volumetric flow rate [lt/h], MM_{H_2O} , MM_{HCl} , MA_{Cl} , $MM_{NH_4^+}$, MM_{NH_4OH} , MM_{OH^-} and MA_{Fe} are the component molar mass [g/mol], α is the fixed drag solution percentage and $C_{Fe^{3+}}^{MRB}$ is the iron concentration in *Metals Rich Brine*.

For the characterisation of the reactive precipitator outlet solution, $1-\alpha$ is used. This stream is carried to the Brine MD where water is recovered and then, added to the *Process Water*. The Brine MD is designed considering that a maximum allowable ammonium chloride concentration of 350 g/lt in the MD outlet stream is permitted due to the salt solubility limit.

RESULTS OF THE MODEL

A parametric analysis of the model was performed varying the main process parameter, specifically the outlet hydrochloric acid concentration in the *Waste Acid Solution* from the pickling tank. In particular, three case-studies have been considered by fixing the HCl concentration in the pickling bath to 80, 100 and 120 g/lt and imposing the corresponding iron concentration from the Kleingarn curve. Results were obtained considering constant values of the evaporation flux and inlet/outlet entrainment rate in the pickling tank.

Process streams flow rates

The flow rate of all the considered streams increases as the HCl concentration in the *Waste Acid Solution* increases from 80 to 120 g/lt, as shown in Figure 4.

Waste Acid Solution flow rate increases from 13.2 to 18.0 lt/h as the iron concentration decreases according to the pickling curve (see Eq. 4). Also the *Recovered Acid Solution* flow rate increases, from 13.6 to 19.0 lt/h, because higher is the *Draw Solution* due to the assumption of WAS/DS = 1. Moreover, for this assumption, also the *Process Water* flow rate raises, from 7.6 to 11.6 lt/h, due to the closure of the overall mass balance.

Another important parameter involved in the model process is the inlet of *Acid Make-up* in the pickling tank, necessary to restore the HCl consumed in the pickling reactions and lost in *Metal Rich Brine* stream. Considering that HCl consumed in the pickling tank is constant as manufacturing steel inlet is constant, the variation of the *Make-Up* volumetric flow rate mainly depends on the different quantity of HCl in the *Metals Rich Brine* stream. Thus, as *MRB* flow rate increases from 12.9 to 17.0 lt/h, also the *MU* stream increases (6.4-6.7 lt/h).

Finally, considering the assumption of steady-state operating mode, the higher is the *WAS* flow rate, the higher is the *Recovered Pickling Solution* (8.8 to 12.7 lt/h) due to the closure of the pickling unit mass balance.

Definitely, for a waste acid solution stream to be treated of 13-18 lt/h, about 6.5 lt/h of *Acid Make-Up* are required to keep the HCl concentration constant at the optimal condition in the pickling tank.

HCl and Fe concentrations

Varying HCl concentration in the *WAS*, clearly, influences acid and iron concentrations along process units. In the pickling stage, where optimal conditions are set accordingly to the Kleingarn curve, a growing HCl in *WAS* concentration leads to iron concentration decreasing. In the *RAS*, and consequently, in the *RPS*, C_{Fe} trend is increasing mainly due to the increase of the membrane area (Fig. 5a). In fact, this value raises from 0.8 to 1.5 m² due to the requirement meeting of the $\Delta C_{min,d} = 3$ g/lt.

For what concern the HCl, the higher is the concentration in *WAS* (80-120 g/lt), the higher is in the *RAS* (71.6-110.5 g/lt) as a higher acid flow rate through the membrane is observed (0.9-1.9 kg/h). Consequently, also the acid reintroduced in the pickling tank in the *RPS* stream is increased (100.5-146.6 g/lt, Fig. 5a).

Similar considerations can be done for the *DS* stream, where the HCl concentration increases due to the higher acid flow rate through the membrane in the MD unit (0.09-0.24 kg/h).

In the *MRB*, HCl and Fe concentrations depend on the components passage through the membrane in DD unit and, as a consequence, the increasing trend of the acid and the decreasing trend of the iron in the *WAS* are found also in the *MRB* (Fig. 5b).

Recovery Ratio

The acid recovery ratio *RR* that occurs in the Diffusion Dialysis unit is calculated by the following equation:

$$RR (\%) = \frac{F_{HCl,d}^{out} - F_{HCl,d}^{in}}{F_{HCl,r}^{in}} \times 100 \quad (28)$$

where $F_{HCl,d}$ and $F_{HCl,r}$ are the hydrochloric acid molar flow rate of the diffusate and retentate solutions and the apices *in* and *out* indicate the inlet and outlet from the DD channel, respectively. The Recovery Ratio slightly increases from 80 to 86% due to an increment of the HCl flux through the membrane (1.12-1.26 kg/h·m²).

Reactive precipitation stage

The oxidant and alkaline reactants volumetric flow rates are correlated to the iron content in the reactive precipitation unit inlet stream (*Metal Rich Brine*). As the HCl increases in the *WAS*, considering the Fe concentration decreasing and the *MRB* volumetric flow rate increment, a higher mass flow rate of iron has to precipitate (1.68-1.71 kg/h). As a consequence, as shown in Table 1, higher reagents consumptions, i.e. hydrogen peroxide and ammonium hydroxide solutions, are required. Moreover, an increasing iron content leads to higher *Metals sludge* flow rates.

Concerning the Brine Membrane distillation, as shown in Table 2, the MD inlet volume flow rate increases (12.5-15.4 lt/h) as the *Metals Rich Brine* flow rate increases. On the other hand, NH₄Cl concentration decreases (188-160 g/lt) due to a dilution effect for the *MRB* flow rate increment. As expected, Brine MD outlet streams flow rates raise as the inlet MD increases. The values reported in Table 2 are calculated by imposing the maximum allowable ammonium chloride concentration of 350 g/lt, as stated above.

Definitely, for a waste acid solution stream to be treated of 13-18 lt/h, about 3.2 lt/h of hydrogen peroxide and about 4.5 lt/h of ammonium hydroxide solutions are required to obtain about 3.2 kg/h of iron(III) hydroxide product. In addition, the water permeate stream recovered from the Brine MD of about 7 lt/h can contribute for the 70% to the process water stream required in the Demo.

CONCLUSIONS

This work focuses on a novel approach for the recovery and optimisation of pickling solutions for hot-dip galvanising plants, with a specific focus on a case study relevant to the hot-dip galvanizing plant of TecnoZinco (Palermo, Italy). The simulation tool, design and operational sensitivity analysis of a demonstration pilot plant

to be installed within the EU-funded ReWaCEM project activities (www.rewacem.eu) is presented. Starting from an accurate data mining, a Process Flow Diagram (PFD) of an integrated process for continuous regeneration of pickling solutions is proposed and analysed by the purposely implemented process simulator. The parametric analysis shows the effect of increasing the hydrochloric acid concentration in the *Waste Acid Solution* on the main streams of the process. All operational parameters are monitored, including HCl and Fe concentrations, performance indicators and membrane area requirements.

A high acid recovery (higher than 80%) is obtained in the DD, while keeping a low iron leakage (below 4-5%). Even if a make-up of fresh acid is still necessary in the integrated process, the operation of the integrated system is performed under optimal conditions for the pickling baths by continuously controlling the concentration of free acid and iron in the pickling solutions.

The advantage of the reactive precipitation stage relies in the obtainment of pure iron hydroxide as by-product. Moreover, the concentrated solution exiting from the final MD unit can be reused in the fluxing baths of the pickling plant thus further integrating the whole process with savings in chemicals and process water. Successful operation of the integrated process will allow to avoid the standard periodic steps of withdrawing and refilling pickling baths at the same time guaranteed the pickling operation under optimal conditions, thus reducing pickling time and enhancing the overall system effectiveness.

ACKNOWLEDGMENTS

This work has been funded by EU within the ReWaCEM project (Resource recovery from industrial waste water by cutting edge membrane technologies) – Horizon 2020 program, Grant Agreement no. 723729. www.rewacem.eu

REFERENCES

- [1] Regel–Rosocka, M. (2010) Journal of Hazardous Materials, 177, 57-69
- [2] Tomaszewska, M., Gryta, M., Morawski, A.W. (2001) Separation and Purification Technology, 22-23, 591-600
- [3] Luo, J., Wu, C., Xu, T., Wu, Y. (2011) Journal of Membrane Science, 366, 1-16
- [4] Xu, J., Lu, S., Fu, D. (2009) Journal of Hazardous Materials, 165, 832-837
- [5] Jatuphaksamphan, Y., Phinichka, N., Prapakorn, K. and Supradist, M. (2010) Journal of Metals, Materials and Minerals, 20(1), 33-39
- [6] Campano, B.R. The Kleingarn Regenerated Spent Acid at Increasing Ferrous (Fe^{+2}) and Ferric (Fe^{+3}) Chloride Content, <https://www.finishing.com/library/campano/kleingarn.pdf>
- [7] Lalibertè, M. and Cooper, W. E. (2004) Journal of Chemical & Engineering Data, 49, 1141-1151
- [8] Gueccia, R., Randazzo, S., Chillura Martino, D., Cipollina, A. and Micale, G., Experimental investigation and modelling of diffusion dialysis for HCl recovery from waste pickling solution, in preparation

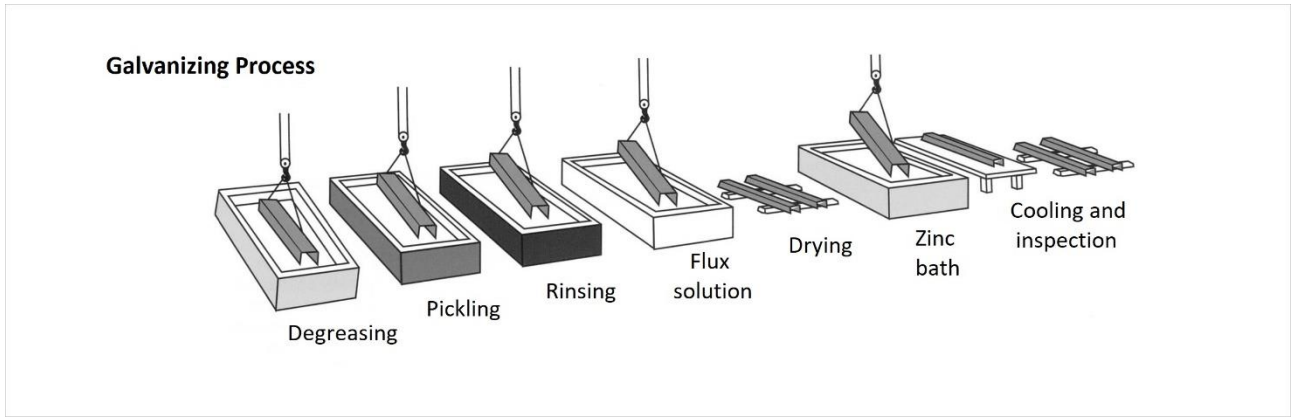


Figure 1. Hot-dip galvanizing process steps at Tecnozinco plant

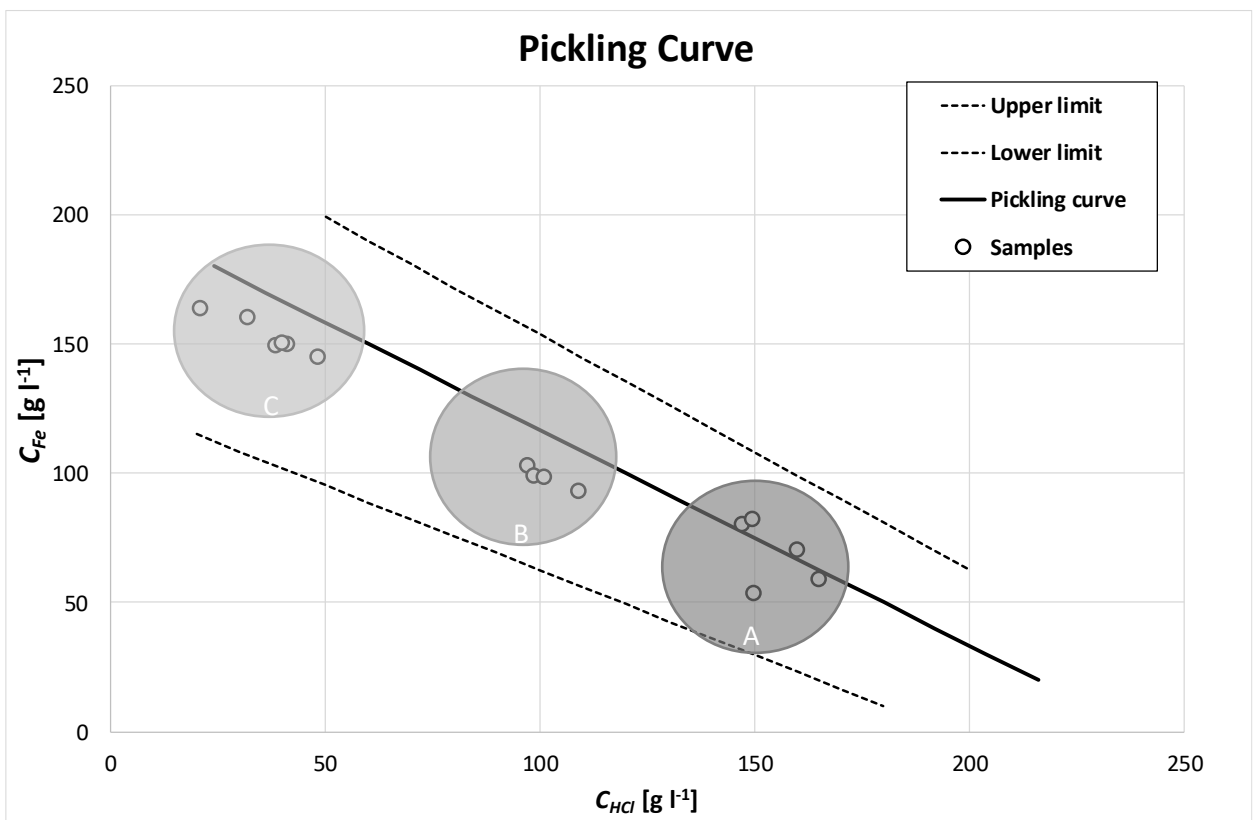


Figure 2. Kleingarn curve. Fe concentration vs. HCl concentration is reported. (—) represents the optimum pickling line; (- - -) delimited the pickling active region. Tecnozinco recent sample compositions are also reported in the figure.

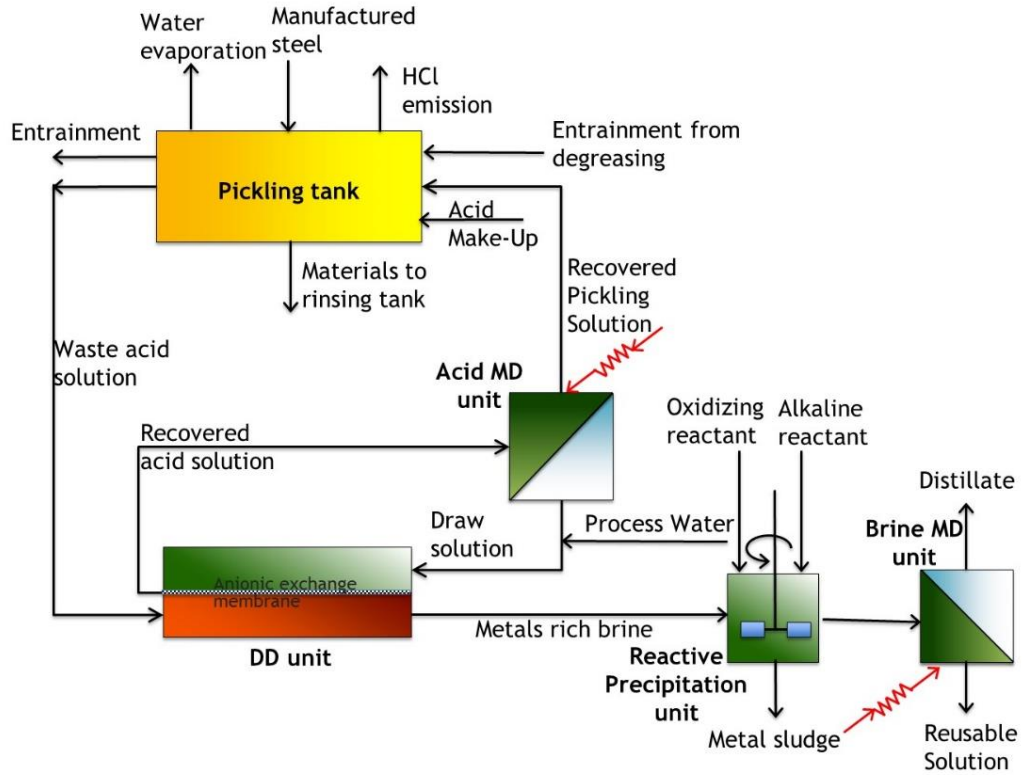


Figure 3. Process Flow Diagram (PFD) of the membrane integrated process for HCl and metals recovery

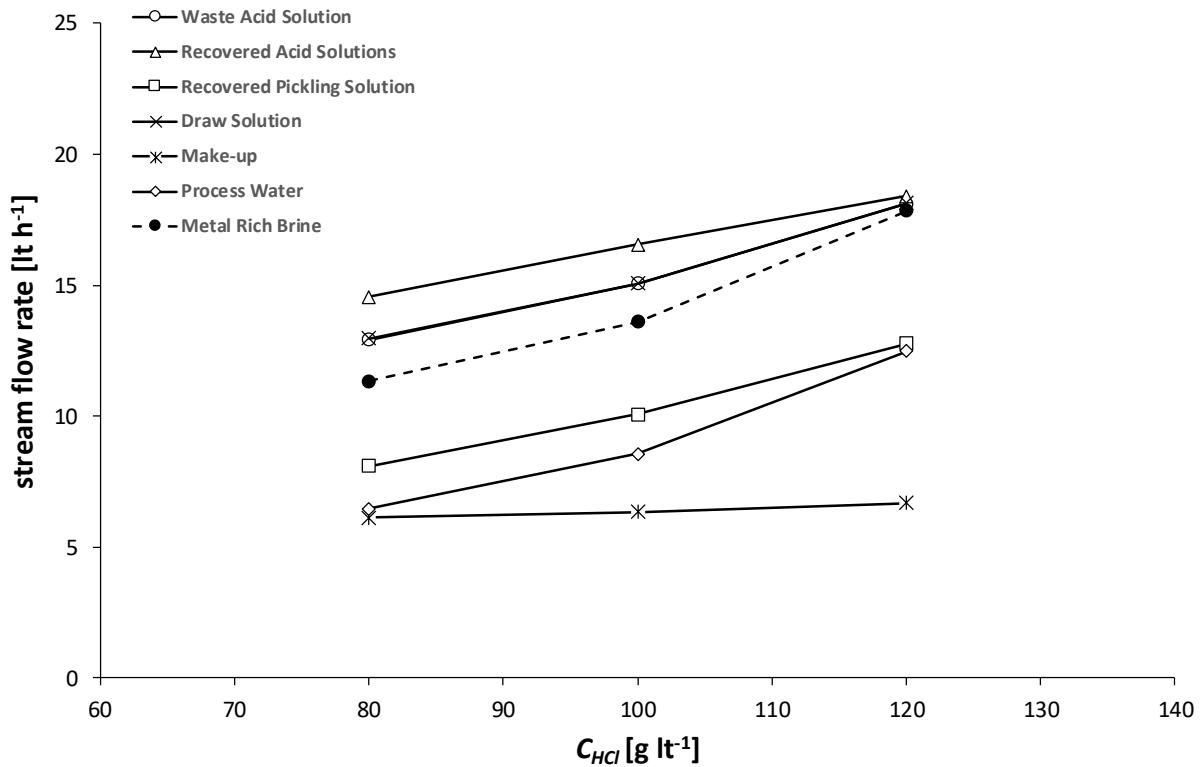
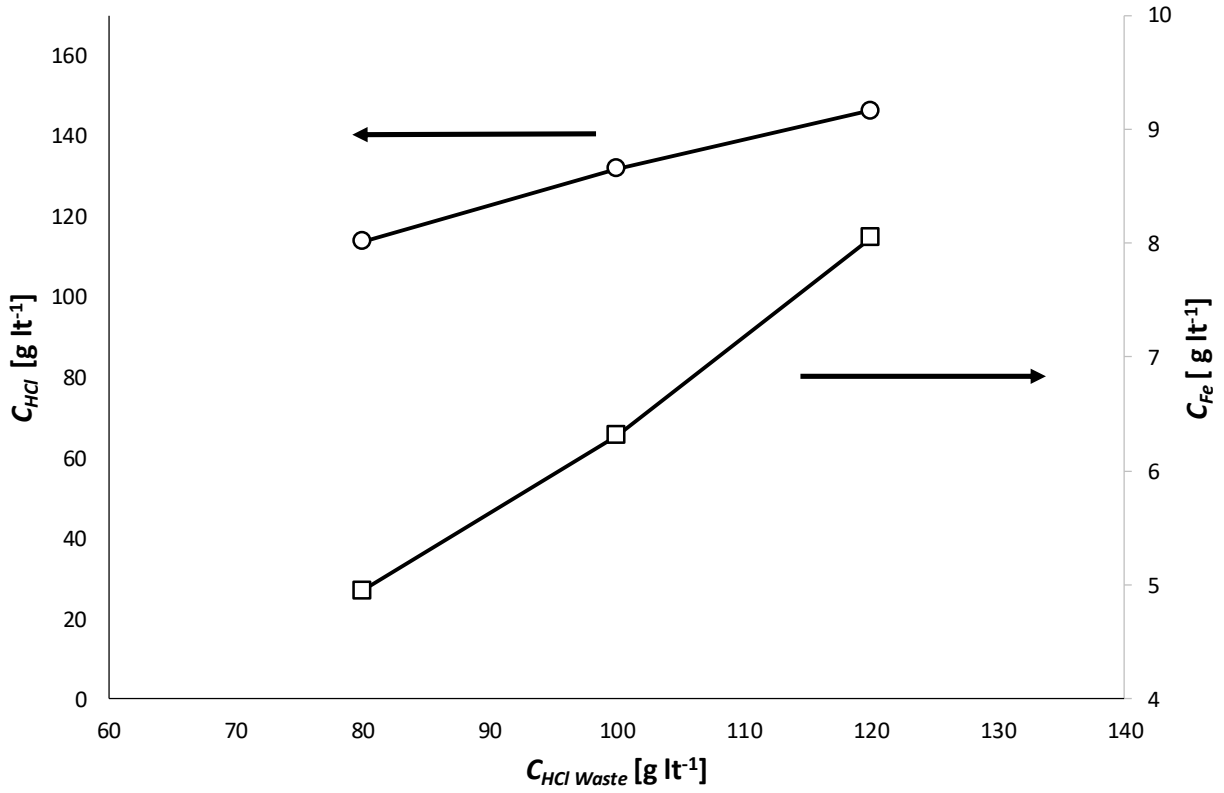
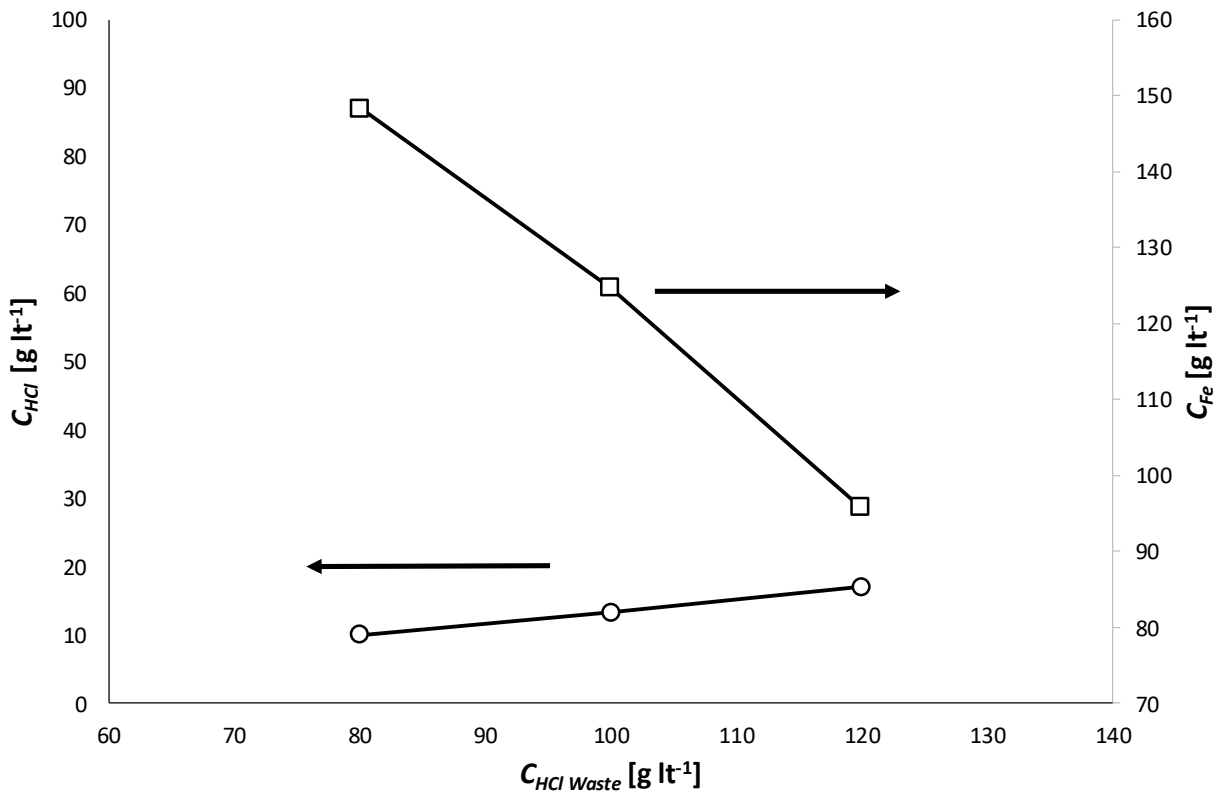


Figure 4. Waste Acid Solution, Recovered Acid Solution, Recovered Pickling Solution, Acid Make-Up and Process Water flow rates as a function of C_{HCl} in the Waste Acid Solution. $WAS/DS = 1$; ΔC_{min-d} in DD = 3 g/L. Evaporated flux and inlet and outlet entrainment solutions are constant.



(a)



(b)

Figure 5. HCl and Fe concentration in the *Recovered Pickling Solution* (a) and in the *Metal Rich Brine* (b) as a function of C_{HCl} in the *Waste Acid Solution*. $WAS/DS = 1$; $\Delta C_{min-r-d}$ in *DD* = 3 g/L.

Table 1. Main streams flow rates as a function of C_{HCl} in the reactive precipitation stage (pH of the outlet stream = 4, drag solution in precipitate = 35%)

		$C_{HCl,waste}$ [g/lt]		
		80	100	120
Oxidant	W_{tot} [kg/h]	3.1	3.2	3.2
Alkaline reactant	W_{tot} [kg/h]	4.4	4.5	4.6
Metals sludge	W_{tot} [kg/h]	10.3	11.2	12.0

Table 2. Main streams flow rates as a function of C_{HCl} in the Brine-MD

	$C_{HCl,waste}$ [g/lt]	Q [lt/h]	C_{NH4Cl} [g/lt]	ρ [g/lt]
Inlet MD	80	12.5	188	1060
	100	14.1	168	1053
	120	15.4	160	1050
Outlet MD	80	6.7	350	1103
	100	6.8	350	1103
	120	7.1	350	1103
Permeate	80	5.6	0	1000
	100	7.2	0	1000
	120	8.2	0	1000