Hydrochloric Acid and Metals Recovery from Pickling Solutions by Integrated Membrane Processes: modeling and design

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

Dipartimento di Ingegneria, Università di Palermo – Viale delle Scienze ed.6, 90128 Palermo, Italy
Corresponding author: Tel: +3909123863779; E-mail: serena.randazzo@unipa.it

Abstract

Hydrochloric acid pickling is a common practice in steel manufacturing industry. During the process, acid is consumed to dissolve surface oxides and metals ions are accumulated in the solution, which becomes less effective with time. Continuous regeneration of pickling solutions enhances process rate and performance, but also minimises the highly expensive and environmentally risky wastewater disposal. In this way, refilling pickling baths with fresh acid (as in conventional operation) can be avoided and can be carried out continuously under the optimal working conditions. The recovery of valuable substances (e.g. metal hydroxide or salts solution) can be an additional benefit. Continuous treatment and regeneration of pickling solution can be accomplished by coupling diffusion dialysis (DD) and membrane distillation (MD) technologies. Moreover, a reactive precipitation unit can be used to precipitate and separate iron ions from zinc-rich solution, in order to recover valuable products and a recyclable fluxing stream (ammonium and zinc chlorides solution).

In the present work, a steady state process simulator for the integrated process has been developed. The aim is to design and simulate the operation of a small pilot-scale unit to be installed and operated

within a real hot-dip galvanizing plant. A parametric analysis of the process has been performed varying the hydrochloric acid concentration in the integrated process inlet stream.

Keywords: Process simulator; Industrial wastewater; Ion-Exchange membranes; Hydrochloric acid concentration; Steel manufacturing

1. 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 metal 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 ions and the consumption of free acid in the solution. When hydrochloric acid is used, ferrous chloride is produced during the pickling treatment, reaching Fe^{2+} concentrations up to 200-250 g l^{-1}, while the acid concentration decreases by 75-85%. A pickling bath in this condition is considered spent (Regel-Rosocka, 2010) 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 concentrated 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 environmental footprint and costs. Thus, the recovery of acid is one of the most beneficial steps to reduce the environmental and economic impact.

A conventional method for the disposal of the waste acid solution is the direct discharge after neutralization by common alkaline reactants. Up to now, several other methods to recover acid from spent pickling solutions have been developed such as cooling and crystallization, evaporation, distillation, thermal decomposition, solvent extraction and membrane separation methods (Leonzio, 2016; Machado et al., 2017; Regel-Rosocka, 2010; Xu et al., 2009). Concerning HCl, as an example, regeneration by spray roasting (the so-called "Ruthner process") or fluidized bed process (the so-called KCH technology) is applied at the industrial scale in many plants in the world (Bascone et al., 2016; Regel-Rosocka, 2010).

Waste acid minimization can also be achieved through optimisation of pickling. Some authors studied the pickling rate by the optimal iron/hydrochloric acid concentration ratio in the pickling tank (Kleingarn, 1988; Stocks et al., 2005).

In the present work, the continuous regeneration of pickling solutions is proposed to enhance pickling rate and process performance, recover of valuable compounds (e.g. acid and metals) and reduce industrial wastewater disposal. This process can be accomplished by coupling two different membrane technologies: diffusion dialysis (DD) and membrane distillation (MD). In fact, membrane techniques are considered simple, effective and sustainable and can be easily scaled from small to medium side installations (Regel-Rosocka, 2010).

Diffusion dialysis is a simple membrane separation technique, which can be successfully used for the treatment of waste acid solutions containing even high concentrations of metal ions (Gueccia et al., 2019; Jung Oh et al., 2000; Luo et al., 2013; Palatý and Bendová, 2009; Xu et al., 2009). Thanks to the anionic exchange membrane used in the DD module, separation of acid and metal salts occurs. Membrane distillation (MD) can be used to concentrate hydrochloric acid solutions (Liu et al., 2012; Tomaszewska et al., 1995). In MD a hydrophobic membrane separates two aqueous solutions at different temperature and composition. The different partial pressures at the two membrane sides generate the driving force for the passage of vapour molecules through the microporous membrane and the permeate composition is a function of both the temperature and the composition of the feed (Luo et al., 2011; Tomaszewska et al., 2001). Interestingly, the process can be performed at a feed temperature considerably lower than its boiling point, thus allowing the utilization of waste heat or alternative thermal energy sources (Tomaszewska et al., 2001).

The analysis here presented refers to a specific case study, relevant to the hot-dip galvanizing plant of Tecnozinco (Palermo, Italy). 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. The final aim is to build a small-pilot unit for the acid and metals recovery to be installed and operated in real environment (www.rewacem.eu).

A steady state process simulator for the integrated process has been developed aiming to design and simulate the operation of the pilot unit. A parametric analysis of the process was performed varying

the inlet stream (pickling solution) composition. Results present the expected operating performance of the pilot plant, assessing the technical feasibility of the novel developed process.

2. Processes description

2.1 Hot-dip galvanizing process: main facts

Hot-dip galvanizing process includes several steps. Following the pathway shown in Figure 1, the manufactured steel is first degreased in a bath under action of surfactants, then it is transferred in a pickling tank, washed in a rinsing tank and put in a fluxing bath before drying and galvanizing.
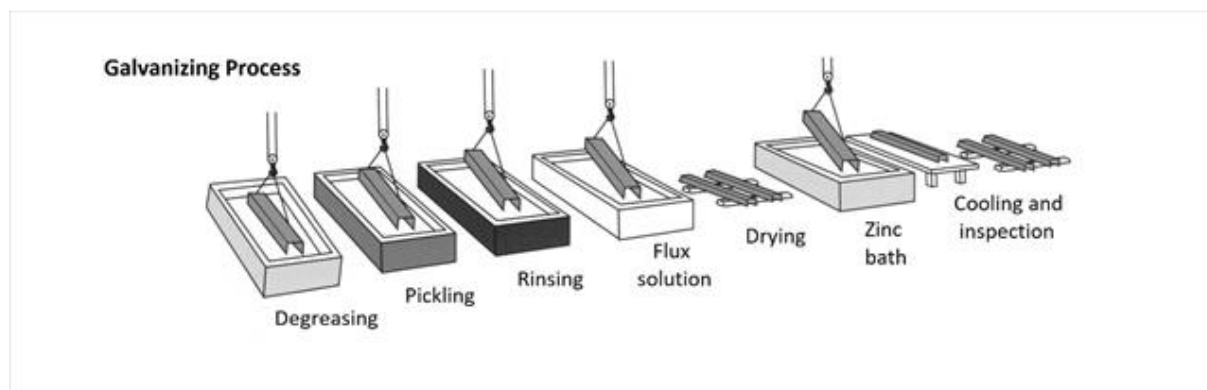

Fig. 1. Sketch of the hot-dip galvanizing process steps at Tecnozinco plant adapted from https://galvanizeit.org/hot-dip-galvanizing/what-is-galvanizing/hdg-process

The fluxing solution contains zinc and ammonium salts to protect the manufactured steel during the drying process and before the immersion in the molten zinc bath and to catalyse zinc covering in this latter step.

Steel pickling is typically performed by immersing the manufactured steel in hydrochloric acid (HCl) bath. The acid dissolves the superficial oxidized layers leading to the formation of iron(II) chlorides in the pickling solution. The kinetic of these reactions is strongly affected by the presence of acid molecules and the iron ions concentration. A specific relationship between the acid and the iron concentration for optimal pickling operation is reported in the literature and known as the *Kleingarn Curve* (Kleingarn, 1988). In Fig. 2, the optimal pickling line and the delimited pickling active region are reported. In addition, also the composition of some representative samples from Tecnozinco pickling baths are

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shown in the figure. Therefore, controlling acid and iron concentrations within the tank increases

pickling rate compared to replacing the entire spent acid bath with fresh acid.
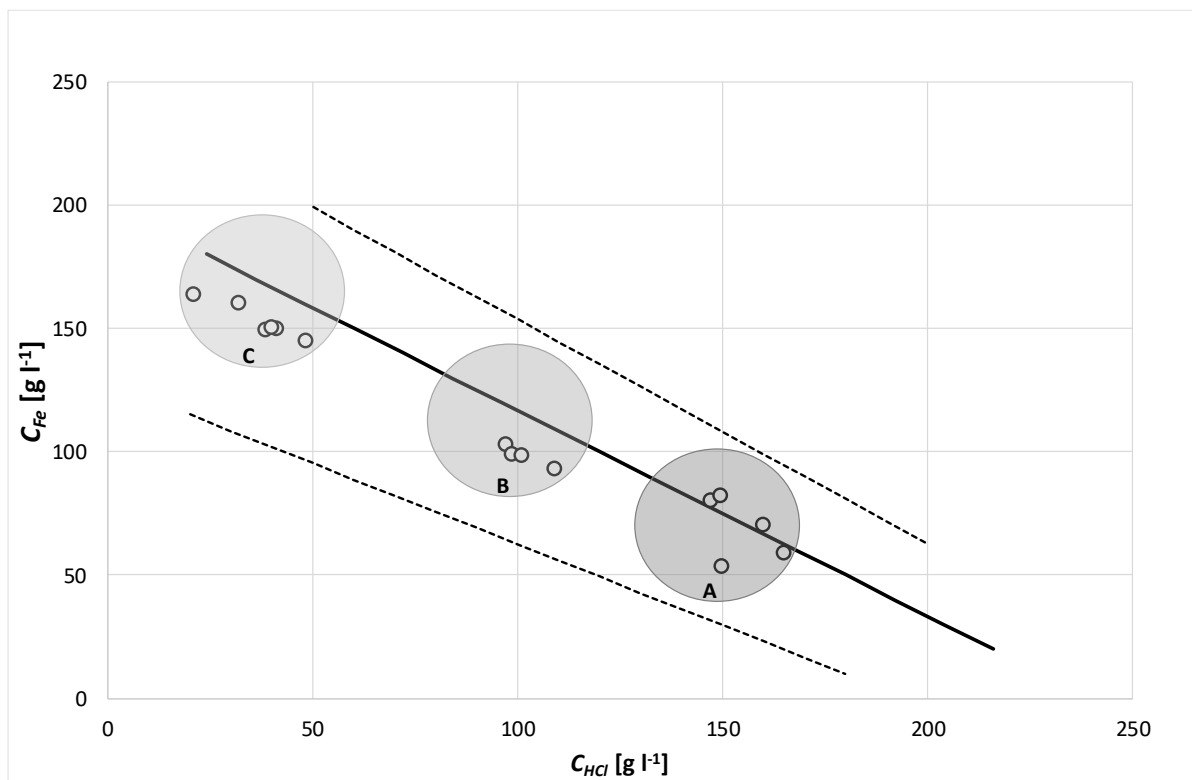
Fig. 2. Graphical representation of the optimal pickling Kleingarn curve (continuous line) (Kleingarn, 1988), with indication of minimum and maximum threshold lines for pickling operation (dashed lines). Empty circles represent the compositions of some real samples from Tecnozinco pickling baths.

Tecnozinco facility uses 7 pickling bathes containing in total more than 350 m³ of acid pickling solution.

The site has a capacity of 20,000 tons per year of treated steel. The acid consumption is approximately

160-240 ton per year. Bathes can be grouped in three classes according to the "pickling power": highly

effective pickling at higher acid concentration and lower iron concentration (HCl 125-170 g l^{-1}, Fe 40-

100 g l^{-1} - area A in Figure 2), intermediate effective pickling at intermediate acid and iron

concentrations (HCl 75-120 g l^{-1}, Fe 80-145 g l^{-1} - area B in Figure 2) and poorly effective pickling at

lower acid concentration and higher iron concentration (HCl 15-60 g l^{-1}, Fe 135-195 g l^{-1} - area C in

Figure 2). Based on periodical analysis of free acidity and iron content, the pickling solution composition

is "adjusted" by spilling part of the solution and subsequent replenishing with water and HCl in order to

remain close to the optimal condition curve.

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^{-1}) and zinc (10-30 g l^{-1}). Disposal costs incurred by Tecnozinco include transportation to a waste treatment plant located in northern Italy (total disposal cost is around 0.15 €/kg, of which 80% for the transport)

2.2 Integrated process description

The proposed integrated process aims at synergistically merging DD and MD processes to keep HCl and iron concentrations in the pickling tank at the optimal values and to separate iron and zinc ions in a reactive precipitation unit producing two valuable by-product streams.

The Process Flow Diagram and relative streams characterization are shown in Figure 3.

Starting from the pickling tank, the outgoing stream, named *Waste Acid solution (WAS)*, after a pre-treatment where particles, oil and surfactants are removed, is fed to the Diffusion Dialysis unit (in the retentate side) in which the recovery of acid occurs. Here, the acid is separated from the metal ions thanks to the anionic exchange membrane, which allows the transport of chlorides driven by a concentration difference to the diffusate compartment, while rejecting large cations in solution. Thanks to their small size and high mobility, H^+ ions can diffuse through the anionic membrane, by means of the so called tunneling mechanism (Luo et al., 2011; Xu et al., 2009). Therefore, the acid is recovered in the diffusate side of the DD unit and separation from salts occurs. Although the membrane should reject 100% of metal ions, non-ideal behavior of real AEM leads to some iron and zinc ions diffusing through the membrane, reaching leakage percentage of 5-10% for iron and up to 50-60% for zinc (Gueccia et al., 2019; Xu et al., 2009). This latter can be actually explained due to the formation of negative Zn^{2+} complexes in solution as $ZnCl_3^-$ and $ZnCl_4^{2-}$, whose diffusion through AEMs is allowed.
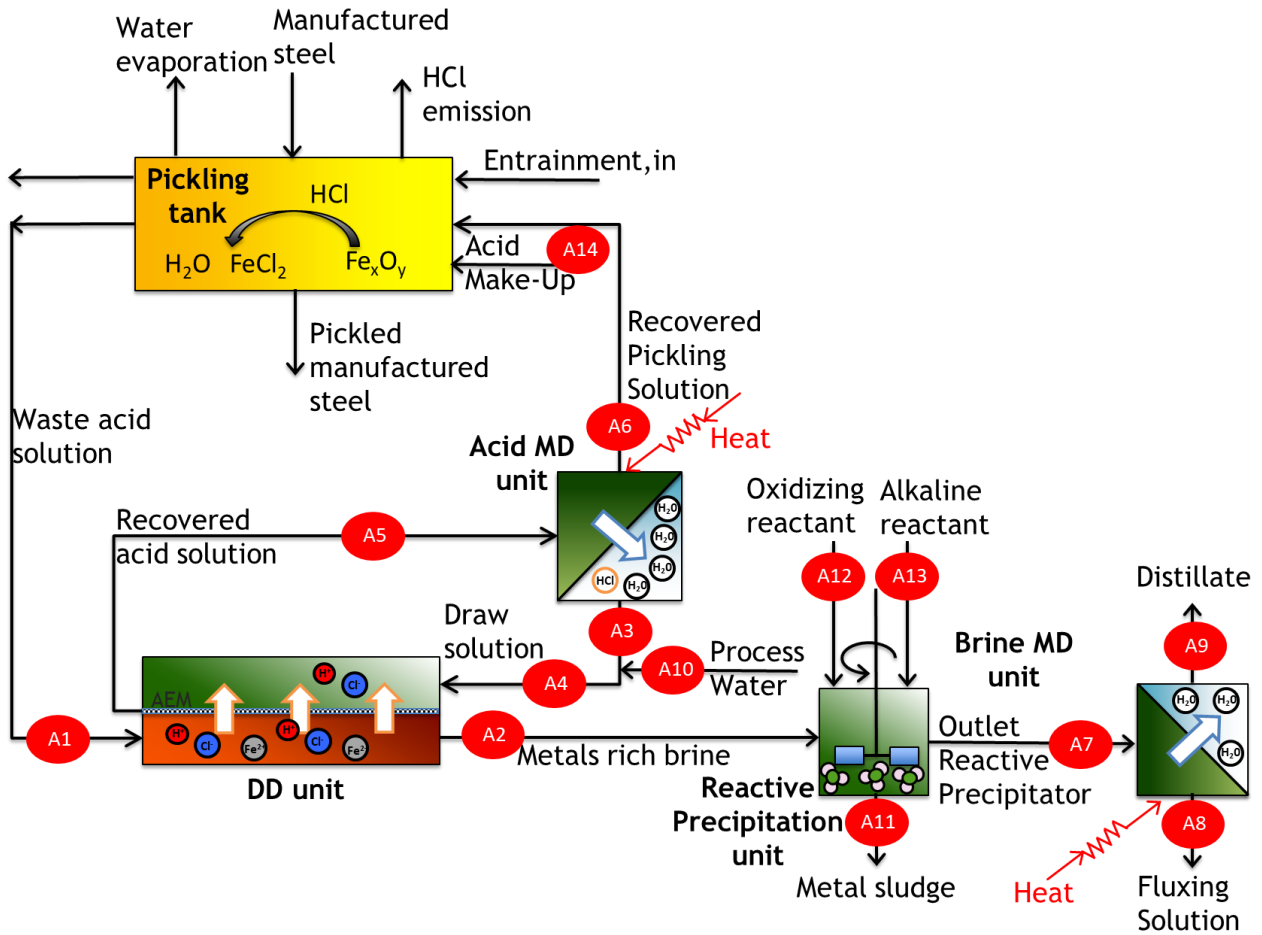
Fig. 3. Process Flow Diagram (PFD) of the membrane integrated process for HCl and metals recovery. Red circles identify all main process streams.

The stream enriched in acid, named *Recovered Acid Solution (RAS)* is sent to the Membrane Distillation (MD) unit, where the acid is concentrated by evaporation/removal of water. In the MD unit, the microporous hydrophobic membrane separates two aqueous solutions at different temperature and composition: the *RAS,* enriched in acid, in the hot side and the *Permeate*, mainly distilled water, in the cold side. In fact, the membrane rejects liquid solution and permits vapour passage from the hot to the cold side, thus mainly water vapour passes and condenses directly in the *Permeate* stream within the cold compartment. As a drawback, also some HCl from the feed can pass to the vapour state and is transported through the membrane especially at high concentrations (Tomaszewska et al., 1995).

The *Permeate* stream from MD is blended with some *Process Water (PW)* and then used as a feed drawing solution to the DD unit (diffusate side), namely the *Draw Solution (DS)*. The stream exiting from MD feed channel, the concentrated *Recovered Pickling Solution (RPS)*, is sent to the pickling tank. The other stream exiting from the DD unit in the retentate side, called *Metals Rich Brine (MRB)*, is a low-acid (0<pH<1) stream enriched in iron and zinc chlorides. This stream is sent to a Reactive Precipitation unit where the acid is neutralized and iron is oxidised and recovered as iron(III) hydroxide, generating the *Metal Sludge (MS)* stream, by addition of H_2O_2 and ammonia solution. As a consequence, a zinc chloride/ammonium chloride solution is produced from this stage, the *Outlet Reactive Precipitator* stream *(ORP)*. Finally, this salty stream is concentrated in a Brine Membrane Distillation unit where additional water is produced. The two outlets, the *Fluxing* stream and the *Distillate*, can be suitably re-used in the fluxing bath of the hot-dip galvanizing plant and as process water in the integrated process, respectively.

In order to compensate for the acid reacted in the pickling bath and for that lost in the MRB, a *Make-Up (MU)* of fresh acid is needed in the pickling bath to maintain the optimal concentration.

The above-described integrated scheme is a nice example of process integration and raw materials circular use, in which all process streams are recirculated in order to re-use a waste stream from a unit as a feed for another or, more in general, to re-use a produced stream elsewhere in the plant or commercializing it. Thus, an overall recovery of materials and minimization of waste streams can be successfully achieved. Moreover, for the pilot-scale unit installed at Tecnozinco, a recovery of waste heat (necessary for the MD operation) is also planned for enhancing the process sustainability.

3. Modeling the integrated process

A mathematical model able to simulate the integrated system operations was developed and implemented in an Excel spreadsheet with Macros in Visual Basic language.

3.1 Data mining

The first step of the modeling activity was to fix parameters and operative conditions of the pickling process. Looking at the scheme of Figure 4, the main information needed concerns the pickling bath, in particular the inlets of manufactured steel, acid make-up and entrainment from the previous step of degreasing on one side, and the outlets of water evaporation, HCl gas emission and entrainment to the further step of rinsing on the other.
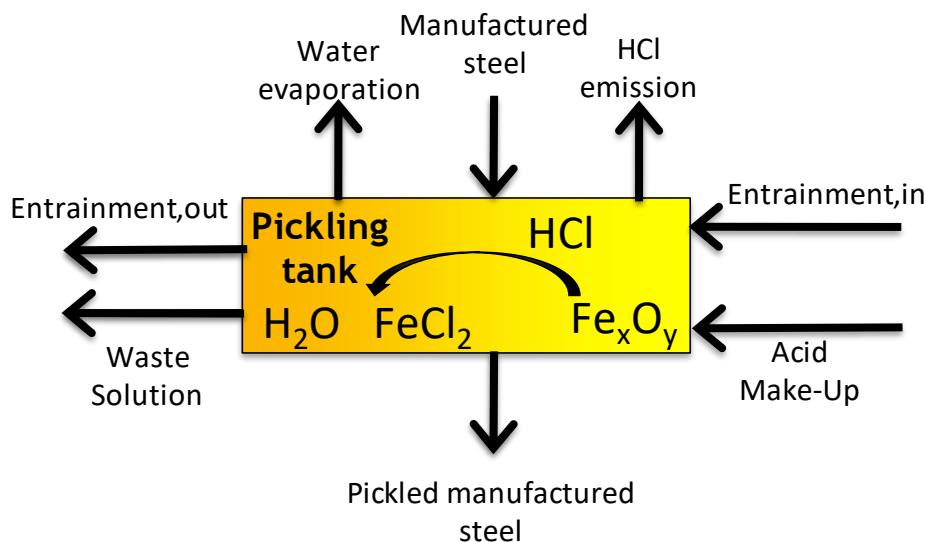
Fig. 4. Scheme of the pickling process at Tecnozinco plant.

In order to estimate the consumption of the acid per ton of manufactured steel, two possible options are possible: using kinetics data from literature or collecting information from available historical statistics of the company. In this work, the latter was selected as starting point. In fact, fixing a time frame of 1 year, real data from Tecnozinco have been collected as shown in Table 1.

Table 1. Operational data on inlet/outlet streams under "traditional" operation of Tecnozinco plant

Manufactured Steel (ton y^{-1})	Acid Make-Up (ton y^{-1})	Exhausted Solution (ton y^{-1})	Entrainment Inlet (l ton^{-1})	Entrainment Outlet (l ton^{-1})	HCl gaseous emission (kg h^{-1})
7410	173	247	2.5	2.5	0.09

In addition to the HCl consumed per ton of manufactured steel, the rate of release of $FeCl_2$ and water from the complexation reactions reported in Eqs. 1 and 2, have been also estimated from mined data.

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With this respect, the main chemical pickling reactions in the presence of corrosion inhibitors were considered (Jatuphaksamphan et al., 2010):

$$Fe_2O_3 + Fe + 6HCl = 3FeCl_2 + 3H_2O \tag{1}$$

$$Fe_3O_4 + Fe + 8HCl = 4FeCl_2 + 4H_2O \tag{2}$$

Assuming that reaction (1) accounts for the 20% and reaction (2) for the 80% of the acid consumption, according to the metal scale composition (Campano, 2012), conversion rates were calculated and linked the following expression:

$$w_i = k_i * w_S \tag{3}$$

where w_i and w_s are mass flow rates 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 and are reported in the following Table 2.

Table 2. Kinetic constants values for the components involved in reactions (1) and (2)

|		
k_{HCl} (kg h^{-1} ton^{-1})	7.6	HCl consumption per ton of steel manufactured
k_{Oxides} (kg h^{-1} ton^{-1})	7.5	Oxides consumption per ton of steel manufactured
k_{Fe} (kg h^{-1} ton^{-1})	5.8	Iron ions released per ton of steel manufactured
k_w (kg h^{-1} ton^{-1})	1.9	Water released per ton of steel manufactured
k_{Cl} (kg h^{-1} ton^{-1})	7.4	Chloride ions released per ton of steel manufactured

3.2 Model assumptions

In order to develop the mathematical model the following assumptions were made:

1. The process operates in steady state conditions;

2. The amount of steel manufactured is equal to 3 ton d^{-1};

3. The pickling bath and the reactive precipitator are considered as perfectly stirred reactors (CSTR);

4. The ratio between the DD inlet feed and draw solution volumetric flow rates is fixed to 1;

5. The local ΔC driving force in terms of HCl concentration difference between retentate and diffusate streams in the DD unit can not reach values lower than 3 g l^{-1};

6. The pH of the outlet stream from the reactive precipitator is fixed to 4;

7. The *Metals Sludge* exiting the reactive precipitator contains 35% of the total solution outgoing from the reactive precipitator (assumption derived from the measurement of residual water content of a filtered cake of sludge).

3.3 Pickling tank

The streams considered for the pickling tank are shown in Fig. 5: *Manufactured Steel*, *Entrainment,in*, Acid *Make-Up* and *Recovered Pickling Solution* as inlets, *Waste Acid Solution*, *Entrainment,out*, water evaporation, HCl emission as outlets and Pickled Manufactured Steel.
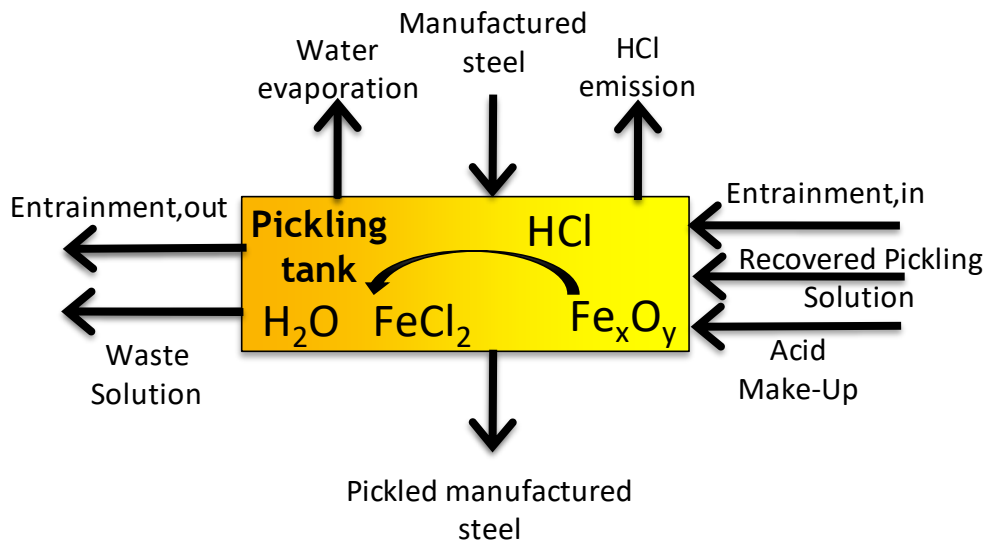
Fig. 5. Pickling process scheme.

The pickling bath is modeled as a continuous stirred-tank reactor (CSTR). As a result, the volumetric flow rate coming from the pickling bath is calculated by Eq. 4:

$$F^{WAS} = \frac{k_{Fe} \cdot w_s + w_{Fe}^{DD} + w_{Fe}^{entr,in} - w_{Fe}^{entr,out}}{C_{Fe}} \tag{4}$$

where F^{WAS} is the *Waste Acid Solution* volumetric flow rate , k_{Fe} is the iron release rate, w_s is the manufactured steel mass flow rate, w_{Fe}^{DD} is the iron mass flow rate arriving with the acid from the whole regeneration process, $w^{entr,in}_{Fe}$ and $w^{entr,out}_{Fe}$ are the iron flow rates related to the streams *Entrainment,in* and *Entrainment,out* arriving from the degreasing and leaving to the rinsing tanks, respectively. C_{Fe} represents the optimal iron concentration corresponding to the HCl concentration and calculated from the Kleingarn Curve (see Fig. 2), as reported in Eq. 5:

$$C_{Fe} = -0.833 \cdot C_{HCl} + 200 \tag{5}$$

To evaluate the process streams mass density, the model developed by M. Lalibertè et al. was adopted (Laliberte and Cooper, 2004). 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:

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

where w_{HCl}^{MU}, w_{HCl}^{MRB} and $w_{HCl}^{entr,out}$ are the hydrochloric acid mass flow rates of the *Make-Up, Metals Rich Brine* and *Entrainment,out* streams, respectively. The $k_{HCl} \cdot w_s$ term concerns the HCl flow rate reacted in the pickling process.

To complete the estimation of the main streams of the integrated system, *Process Water* stream is evaluated by performing a global mass balance using the entire integrated system as control volume (Eq. 7).

$$w^{pw} = w^{MRB} + w^{entr,out} + w^{evap} - w^{MU} - k_{oxides} \cdot w_s - w^{entr,in} \tag{7}$$

where $w^{pw}, w^{MRB}, w^{entr,out}, w^{evap}, w^{MU}$ and $w^{entr,in}$ are the water mass flow rates 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. The $k_{oxides} \cdot w_s$ term concerns the oxides mass flow rate inlet within the manufactured steel in the pickling tank.

3.4 Diffusion Dialysis unit

Concerning the Diffusion Dialysis unit, the streams considered for the integrated process simulation are: *Waste Acid Solution* and *Draw Solution* as inlets, *Recovered Acid Solution* and *Metal Rich Brine* as outlets (see Fig. 6).
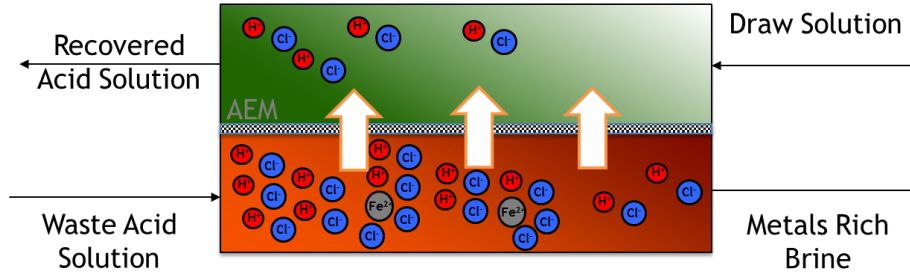
Fig. 6. Diffusion dialysis process scheme.

The equations used in this section were derived from the results obtained from an experimental investigation carried out by some of co-authors (Gueccia et al., 2019). 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, based on a lumped-parameters mathematical description of the DD unit:

$$w_{HCl}^{DD} = A \cdot MM_{HCl}\left[P_{HCl} \cdot \left(\overline{C_{HCl,mol}^{R}} - \overline{C_{HCl,mol}^{D}}\right) + U_s \cdot \left(\overline{C_{Fe,mol}^{R}} - \overline{C_{Fe,mol}^{D}}\right)\right] \tag{8}$$

where w_{HCl}^{DD} is the mass flow rate of hydrochloric acid passing from the retentate to the diffusate side of the DD unit, A is the membrane area, MM_{HCl} is the HCl molar mass, P_{HCl} is the membrane permeability to hydrochloric acid, U_s is the secondary permeability to the passage of acid due to the presence of the chlorides salt. $\overline{C_{HCl,mol}^{R}}, \overline{C_{HCl,mol}^{D}}$ and $\overline{C_{Fe,mol}^{R}}, \overline{C_{Fe,mol}^{D}}$ are the average concentrations of hydrochloric acid and iron in the retentate and in diffusate side, respectively. The expression for P_{HCl} and U_{salt} were derived experimentally (Gueccia et al., 2019) and are reported in Eqs. 9 -10.

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

$$U_{salt} = 9.36 \cdot 10^{-3}\overline{C_{HCl,mol}^{R}} + 3.58 \cdot 10^{-4} \qquad (10)$$

Although the anionic exchange membrane theoretically rejects all iron cations, a small passage of iron chloride is observed (Gueccia et al., 2019; Xu et al., 2009). Therefore, salt diffusion through the AEM membrane was considered by Eq. 11.

$$w_{Fe}^{DD} = A \cdot P_{Fe} \cdot MM_{Fe}\left(\overline{C_{Fe,mol}^{R}} - \overline{C_{Fe,mol}^{D}}\right) \qquad (11)$$

where w_{Fe}^{DD} is the iron mass flow rate passing from the retentate to the diffusate side of the DD unit, A is the membrane area, P_{Fe} is the membrane permeability to the FeCl$_2$, MM_{Fe} is the Fe molar mass, $\overline{C_{Fe,mol}^{R}}$ and $\overline{C_{Fe,mol}^{D}}$ are the iron average concentrations in the retentate and in the diffusate side, respectively. The expression for P_{Fe} was derived experimentally (Gueccia et al., 2019) and it is reported in Eq. 12.

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

in which $\overline{C_{Fe,mol}^{R}}$ is the average iron molar concentration in the retentate side of the DD unit.

Concerning the zinc passage, due to the lack of accurate information on membrane permeability, a leakage percentage of 35% has been assumed, derived from simple and focused experiments carried out at the laboratory scale.

For the water passage two contributions are considered: the osmotic and the drag fluxes through the membrane, where the latter is related to the water solvation shell of transported acid. The osmotic flux J_{os} is calculated by Eq. 13.

$$J_{os} = P_{os} \cdot \Delta\pi = P_{os} \cdot R \cdot T \cdot \rho_w \cdot \left(2 \cdot \overline{\Delta C_{HCl,mol}} + 3 \cdot \overline{\Delta C_{Fe,mol}} + 3 \cdot \overline{\Delta C_{Zn,mol}}\right) \qquad (13)$$

Where P_{os} is the water permeability, $\Delta\pi$ is the average osmotic pressure difference between the two solutions and R is the gas constant, T is the average temperature, ρ_w is the water density, $\overline{\Delta C_{HCl,mol}}$,

$\overline{\Delta C_{Fe,mol}}$ and $\overline{\Delta C_{Zn,mol}}$ are the average concentration differences in the DD of the HCl, Fe and Zn respectively. The expression for P_{os} was derived experimentally:

$$P_{os} = 6.1 \cdot 10^{-3} \overline{C_{HCl,mol}^{R}} + 2.2 \cdot 10^{-2} \tag{14}$$

in which $\overline{C_{HCl,mol}^{R}}$ is the average hydrochloric acid molar concentration in the retentate side of the DD unit.

The drag flux J_{drag} is calculated according to the following equation:

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

where $w_{HCl}^{DD}, w_{FeCl_2}^{DD}$ and $w_{ZnCl_2}^{DD}$ are the HCl, FeCl2 and ZnCl2 mass flow rates passing through the DD membrane, $MM_{HCl,} MM_{H_2O}, MM_{FeCl_2}$ and MM_{ZnCl_2} are the HCl, H2O, FeCl2 and ZnCl2 molar masses. Finally, the overall mass balance and the generic i-component mass balance for the DD unit are reported in Eqs. 16 and 17.

$$w^{DS} + w^{WAS} = w^{MRB} + w^{RAS} \tag{16}$$
$$w_i^{DS} + w_i^{WAS} = w_i^{MRB} + w_i^{RAS} \tag{17}$$

where w^{DS}, w^{WAS}, w^{MRB} and w^{RAS} are the total mass flow rates of the *Draw Solution*, *Waste Acid Solution*, *Metals Rich Brine* and *Recovered Acid Solution* streams, while the subscript *i* indicates the i-component (e.g. FeCl2, HCl, ZnCl2).

3.5 Membrane Distillation unit

With regard to Membrane Distillation unit, the streams considered for the simulation are: *Recovered Acid Solution* as inlet, *Recovered Pickling Solution and Permeate* as outlets (see Fig. 7).
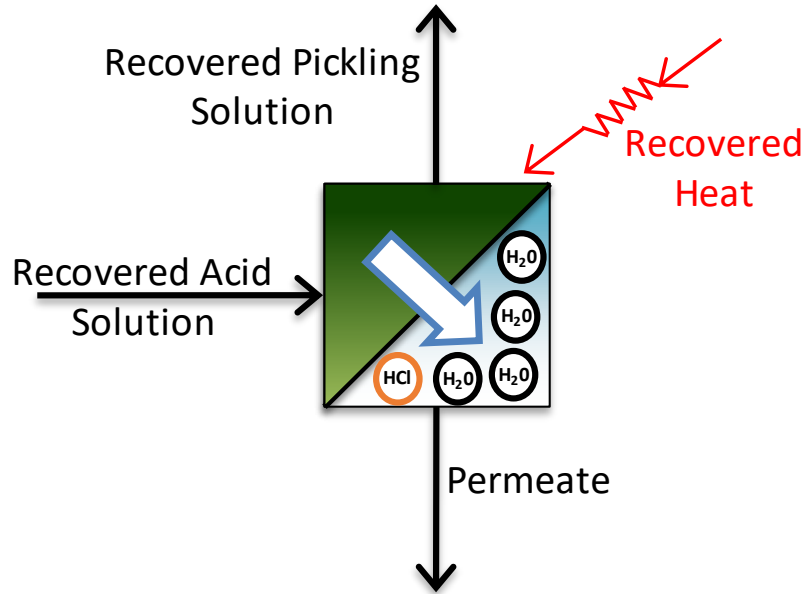
Fig. 7. Membrane Distillation process scheme.

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 (www.reiner-lemoine-stiftung.de/stipendiaten/daniel-winter.html). The values of J_i used in the model are extrapolated from simulations results carried out considering fixed temperature values at both the sides of the membrane. Specifically, in the range of the considered concentrations, and fixing average temperature 75-65 °C, the fluxes are calculated to be: J_w=2.97-3.02 kg m^{-2} h^{-1} and J_{HCl}= 0.08-0.12 kg m^{-2} h^{-1}, for HCl concentration entering with the Recovered Acid Solution varying from 75 to 111 g/l. The overall and for the i-component mass balance for the Membrane Distillation unit are reported in Eqs. 18 and 19:

$$w^{RAS} = w^{RPS} + w^{Perm} \tag{18}$$

$$w_i^{RAS} = w_i^{RPS} + w_i^{Perm} \tag{19}$$

where w^{RAS}, w^{RPS} and w^{Perm} are the total mass flow rates of the *Recovered Acid Solution*, *Recovered Pickling Solution* and Membrane Distillation *Permeate* streams.

3.6 Reactive Precipitation stage

The Reactive Precipitation unit is modeled considering the complete iron precipitation from the solution in the form of iron hydroxide by adding ammonia solution (NH_3 28-30% w/w). Since the iron in solution is mainly present in reduced form (Fe(II)), 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 enough than that of iron(III) hydroxide to obtain the precipitation of only iron(III) at an operating pH range of 3-4. As stated above, in the model assumptions section, *Metal Sludge* was assumed to correspond to the 35% of the total solution outgoing from the reactive precipitator.
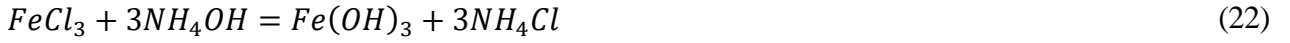
Thus, as shown in Fig. 8, the streams considered here are: *Metal Rich Brine* and *Oxidizing reactant and Alkaline reactant streams* as inlets, *Metal Sludge* and *Outlet Reactive Precipitator* solution stream as outlets.
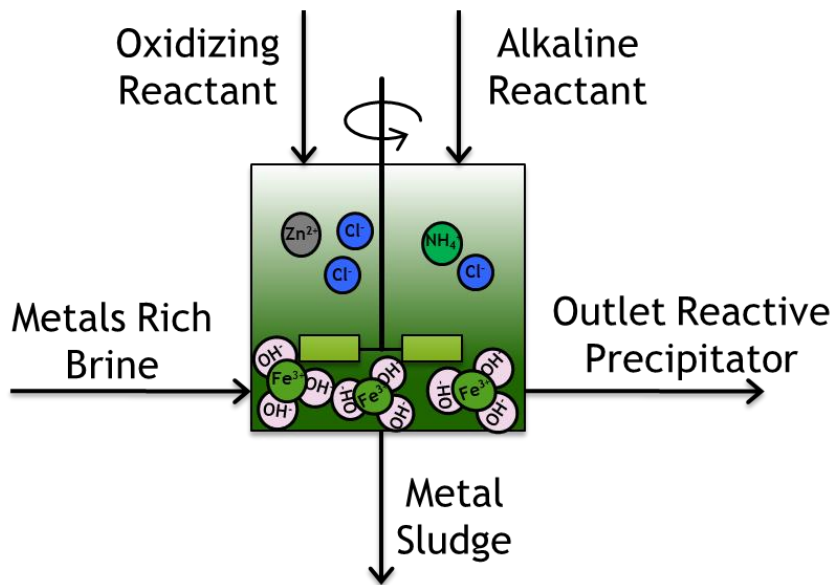
Fig. 8. Reactive precipitator process scheme.

The following reactions are considered in the reactive precipitation process:

$$2FeCl_2 + H_2O_2 + 2HCl = 2FeCl_3 + 2H_2O \tag{20}$$

$$NH_4OH + HCl = NH_4Cl + H_2O \tag{21}$$

$$FeCl_3 + 3NH_4OH = Fe(OH)_3 + 3NH_4Cl \tag{22}$$

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

$$w_{H_2O_2}^{Ox} = \frac{w_{Fe}^{MRB} MM_{H_2O_2}}{2\ MM_{Fe}} \tag{23}$$

where $w_{H_2O_2}^{Ox}$ is the inlet H_2O_2 mass flow rate, w_{Fe}^{MRB} is the Fe mass flow rate in the *MRB*, $MM_{H_2O_2}$

and MM_{Fe} are the molar masses of H_2O_2 and Fe, respectively.

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

$$w_{NH_4OH}^{alk} = \left[(10^{-pH_{in}} - 10^{-pH_{out}}) \cdot F^{WAS} + 3 \cdot \frac{C_{Fe} \cdot F^{WAS}}{MM_{Fe}} \right] \cdot MM_{NH_4OH} \tag{24}$$

where $w_{NH_4OH}^{alk}$ is the NH_4OH mass flow rate in the alkaline reactant stream, pH_{in} and pH_{out} are the

inlet and outlet pH of the solution, F^{WAS} is the *WAS* volumetric flow rate, C_{Fe} is the iron molar

concentration, MM_{Fe} and MM_{NH_4OH} are the iron and NH_4OH molar masses.

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

$$w_{H_2O}^{MS} = \left[(10^{pH_{in}} - 10^{pH_{out}}) \cdot F^{MRB} \cdot MM_{H_2O} + w_{H_2O}^{MRB} + w_{H_2O}^{alk} \right] \cdot \alpha \tag{25}$$

$$w_{HCl}^{MS} = \left[w_{HCl}^{MRB} - (10^{pH_{in}} - 10^{pH_{out}}) \cdot F^{MRB} \cdot MM_{HCl} \right] \cdot \alpha \tag{26}$$

$$w_{Cl}^{MS} = \alpha \cdot w_{Cl}^{MRB} + (w_{HCl}^{MRB} - w_{HCl}^{MS} - w_{HCl}^{out}) \cdot \frac{MM_{Cl} \cdot \alpha}{MM_{HCl}} \tag{27}$$

$$w_{NH_4}^{MS} = w_{NH_4OH}^{alk} \cdot \alpha \cdot \frac{MM_{NH_4}}{MM_{NH_4OH}} \tag{28}$$

$$w_{OH}^{MS} = \frac{3 \cdot C_{Fe}^{MRB} \cdot F_{MRB} \cdot MM_{OH}}{MM_{Fe}} \tag{29}$$

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_{HCl}^{out}, $w_{NH_4}^{MS}$ and $w_{NH_4OH}^{alk}$, w_{OH}^{MS} are

the mass flow rates 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_{out} are the inlet and outlet pH of the solution, F^{MRB}

is the *MRB* volumetric flow rate, MM_{H_2O}, MM_{HCl}, MM_{Cl^-}, MM_{NH_4}, MM_{NH_4OH} MM_{OH} and MM_{Fe} are

the molar masses, α is a coefficient to calculate the flow rate of solution trapped in the humid cake as a % of the outlet solution flow rate (fixed to 35%) and C_{Fe}^{MRB} is the iron concentration in *Metals Rich Brin*e.

Regarding the *Outlet Reactive Precipitator* stream, the mass flow rates of each i-component (i.e. H_2O, HCl, Cl^-, NH_4^+) can be calculated by the following equation:

$$w_i^{ORP} = \frac{w_i^{MS}}{\alpha} \cdot (1 - \alpha) \tag{30}$$

3.7 Brine Membrane Distillation unit

Regarding the Brine MD, the streams to be characterized are: *Outlet Reactive Precipitator* stream as inlet and *Fluxing solution* and *Distillate* as outlets (see Fig. 9).
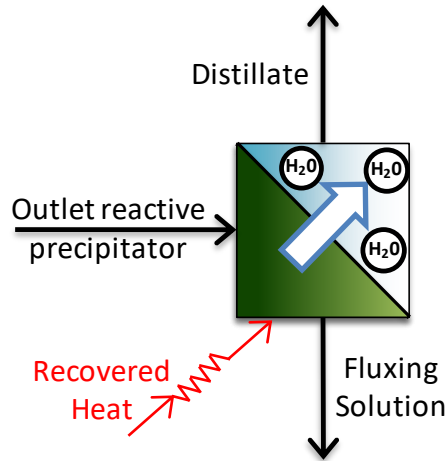
Fig. 9. Brine Membrane Distillation process scheme.

The Brine MD is designed considering that a maximum allowable ammonium chloride concentration of 350 g l^{-1} in the MD outlet stream is permitted due to the salt solubility limit.

The overall and for the i-component mass balance for the Membrane Distillation unit are reported in Eqs. 31 and 32:

$$w^{ORP} = w^{Dist} + w^{FS} \tag{31}$$

$$w_i^{ORP} = w_i^{Dist} + w_i^{FS} \tag{32}$$

where w^{ORP}, w^{Dist} and w^{FS} are the total mass flow rates of the *Outlet Reactive Precipitator* solution, *Distillate and Fluxing Solution* streams.

4. Results of the model

A parametric analysis of the process was performed by varying the main operating parameter, specifically the 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 to 80, 100 and 120 g l^{-1} and imposing the corresponding iron concentration from the Kleingarn curve. It is worth noting that values of evaporation flux and inlet/outlet entrainment rate in the pickling tank were considered constant (as reported in table 1) for the three analysed scenarios.

As a reference case, the streams reported in the process flow diagram of Fig. 3 have been characterized considering the optimal HCl concentration of 100 g/l. The relevant streams properties are reported in Table 3, while the following paragraphs show how the variation of optimal HCl and Fe concentration in the pickling baths, can affect flow rate, composition and performance parameters of the main integrated process stages.

**Table 3.** PFD streams characterization

Stream	w	F	C_{HCl}	$C_{Fe^{2+}}$	$C_{Zn^{2+}}$	C_{NH_4Cl}	C_{NH_4OH}	$C_{H_2O_2}$
	kg h^{-1}	l h^{-1}	g l^{-1}	g l^{-1}	g l^{-1}	g l^{-1}	g l^{-1}	g l^{-1}
A1	19.6	15.3	100	117	8.27	0.0	0.0	0.0
A2	18.6	15.2	14.1	112	5.42	0.0	0.0	0.0
A3	5.25	5.19	32.6	0.0	0.0	0.0	0.0	0.0
A4	15.3	15.3	11.1	0.0	0.0	0.0	0.0	0.0
A5	16.3	15.4	96.5	5.85	2.88	0.0	0.0	0.0
A6	11.0	10.2	129	8.82	4.34	0.0	0.0	0.0
A7	14.9	14.1	0.00255	0.0	3.78	168	0.0	0.0
A8	7.47	6.77	0.00531	0.0	7.90	350	0.0	0.0
A9	7.22	7.22	0.0	0.0	0.0	0.0	0.0	0.0
A10	10.1	10.1	0.0	0.0	0.0	0.0	0.0	0.0
A11	11.2*	-	-	-	-	-	-	-
A12	3.56	3.18	0.0	0.0	0.0	0.0	0.0	325

| A13 | 3.95 | 4.44 | 0.0 | 0.0 | 0.0 | 0.0 | 525 | 0.0 |
| A14 | 7.51 | 6.42 | 400 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

*Metals sludge, after filtration, containing 29% iron(III) hydroxide and 71% of spent brine with up to 13% of $ZnCl_2$ and NH_4Cl salts).

4.1 Effect of changing optimal HCl concentration on the main streams flow rates

Flow rates of all considered streams strongly depends on the Fe concentration. In fact, the main process constrain is that all Fe released by the pickling process has to be totally removed via the *MRB*. Thus, the higher the Fe concentration in the pickling bath (i.e. also in the *WAS*), the lower the required flow rate to be treated (see Eq. 4). Conversely, following the Fe-HCl concentration relationship imposed by the Kleingarn curve, the higher the HCl concentration, the higher the flow rate for the main treatment process streams, as shown in Figure 10.
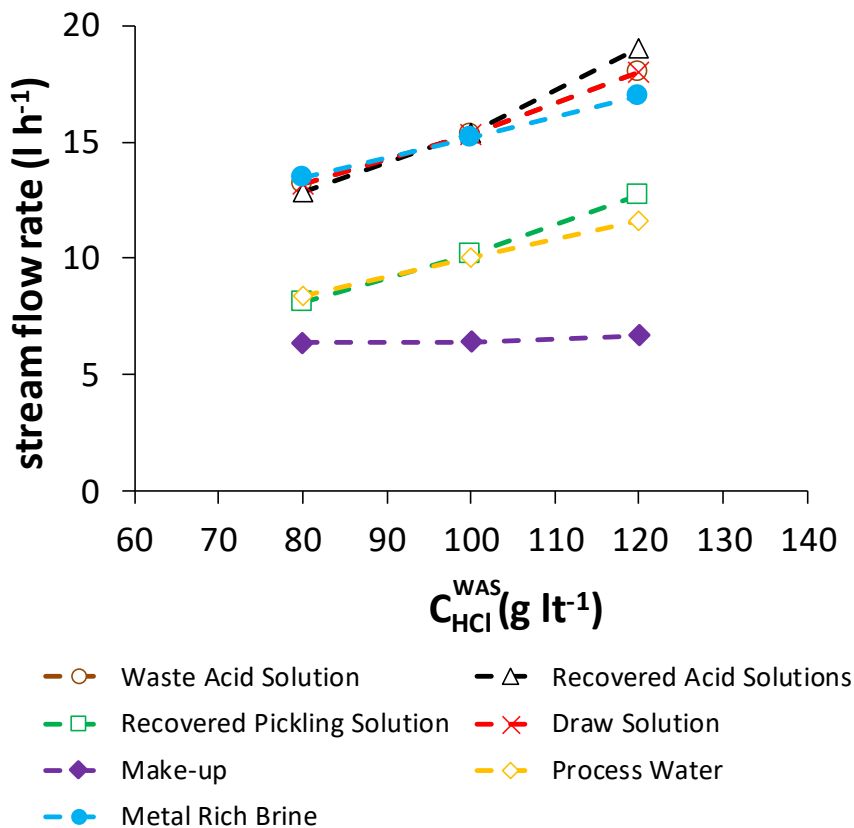
Fig. 10. Streams flow rates as a function of C_{HCl} in the *Waste Acid Solution.*

Waste Acid Solution flow rate increases from 13.2 to 18.0 l h^{-1} as the iron concentration decreases according to the pickling curve. Also the *Recovered Acid Solution* flow rate increases, 12.8 to 19.0 l h^{-1}, due to higher *Draw Solution* flow rate as well as the *Process Water* flow rate raises, from 8.40 to 11.6 l h^{-1}, thus closing the overall mass balance.

Another important parameter involved in the process model is the inlet of *Acid Make-Up* in the pickling tank, necessary to keep HCl concentration constant in the pickling bath. Considering that HCl consumed in the pickling tank is constant (constant manufactured steel inlet quantity), the variation of the *Make-Up* volumetric flow rate mainly depends on the different quantity of HCl lost in the *Metals Rich Brine* stream. Thus, as *MRB* flow rate increases from 13.5 to 17.0 l h^{-1}, also the acid *MU* stream increases (6.37-6.67 l h^{-1}).

Finally, considering the assumption of steady-state operating mode, the higher is the *WAS* flow rate, the higher is the *Recovered Pickling Solution* (8.08 to 12.7 l h^{-1}) due to the closure of the pickling unit mass balance.

4. 2 Effect of changing optimal HCl concentration on the main streams composition

The choice of optimal HCl concentration in the pickling bath and, consequently in the *WAS* strongly influences also acid and iron concentrations along the 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. Thus, the higher is the concentration in *WAS* (80-120 g l^{-1}), the higher in the *RAS* (75.2-111 g l^{-1}) as a higher acid flow rate through the membrane is observed (0.8-1.9 kg h^{-1}) (Fig. 11a). As a consequence, also the acid concentration in the *RPS* stream reintroduced in the pickling tank is increased (104-147 g l^{-1}, Fig. 11b).

However, even if the higher C_{HCl}^{WAS}, the higher iron flux through the DD membrane, the iron concentration in the *Recovered Acid Solution* C_{Fe}^{RAS} and in the *Recovered Pickling Solution* C_{Fe}^{RPS} slightly decrease, due to the increase of the main process flow rate in the system F^{WAS}.
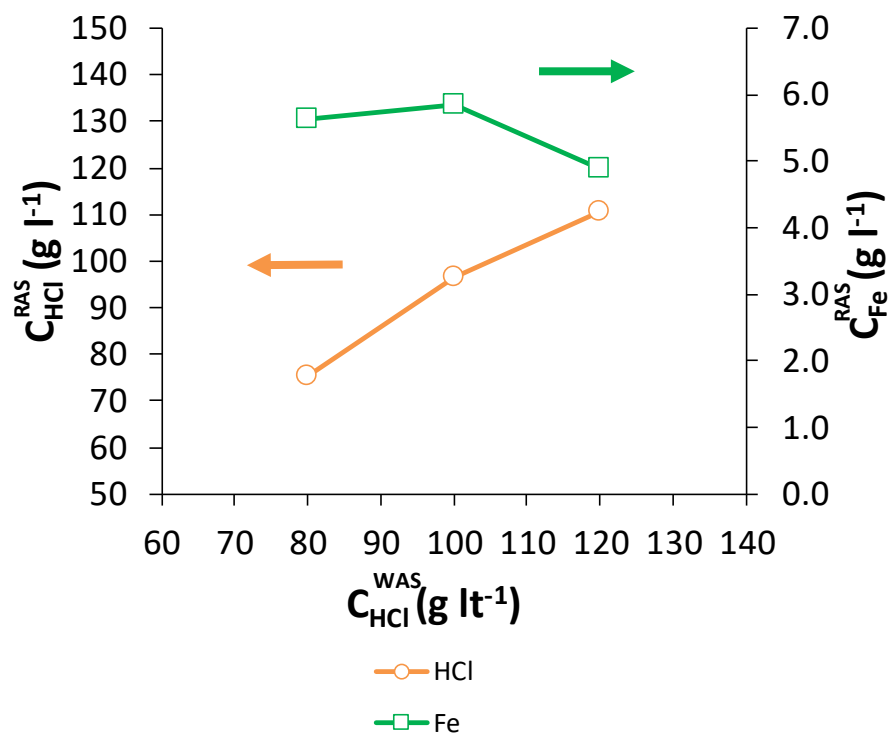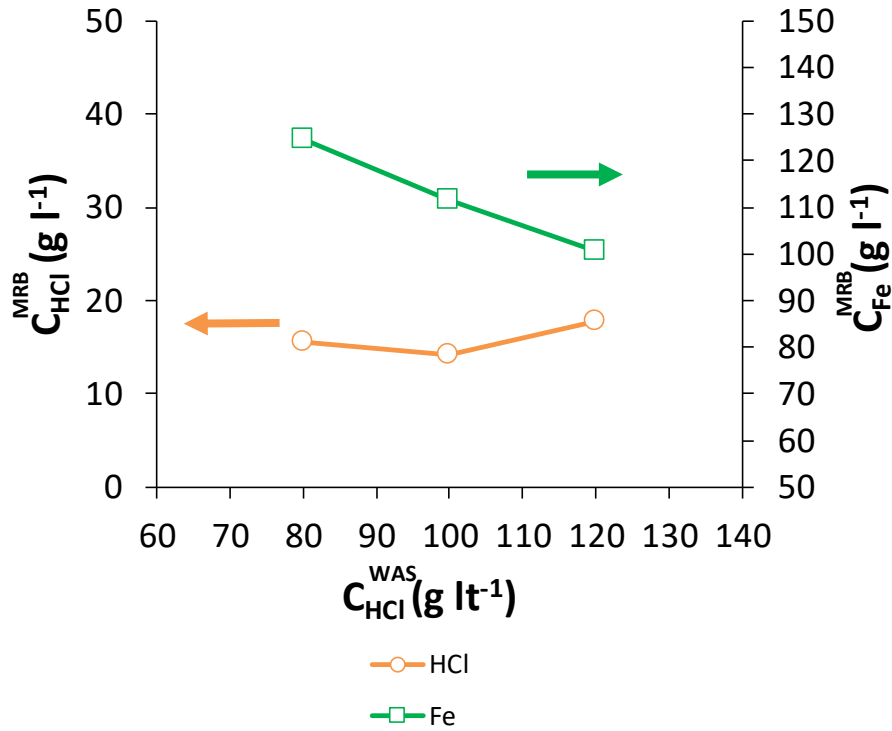
(a)
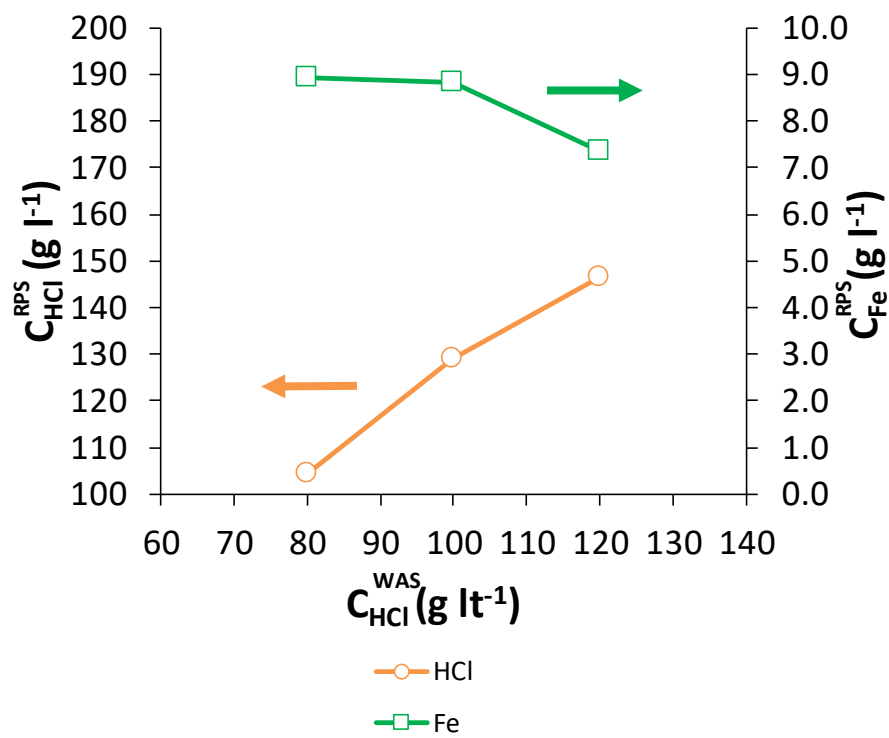
(b)

(c)

Figure 11. HCl and Fe concentrations in the *Recovered Acid Solution* (a), *Recovered Pickling Solution* (b) and *Metal Rich Brine* (c) as a function of C_{HCl} in the *Waste Acid Solution*.

Similar considerations can be done for the *Draw Solution* (*DS*) stream, where the HCl concentration increases due to the higher acid flow rate through the membrane in the MD unit (0.12-0.24 kg h^{-1}). In the *MRB*, HCl and Fe concentrations depend on the components diffusion through the membrane in the DD unit and on the process flow rates and, as a consequence, the increasing trend of the acid in the *WAS* leads to a slightly increase of the HCl concentration and a decrease of the iron concentration in the *MRB* (Fig. 11c).

4.3 Performance parameters in the membrane units

The effect of changing optimal HCl and Fe concentration on the main performance parameters of the membrane units used in the integrated process are discussed in this section.

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

$$RR\ (\%) = \frac{w_{HCl,d}^{out} - w_{HCl,d}^{in}}{w_{HCl,r}^{in}} \cdot 100 \tag{33}$$

where $w_{HCl,d}$ and $w_{HCl,r}$ are the hydrochloric acid mass flow rate of the diffusate and retentate solutions and the superscripts *in* and *out* indicate the inlet and outlet from the DD channel, respectively.

When passing from 80 to 120 g/l optimal HCl concentration in the pickling bath, the Recovery Ratio slightly increases from 80 to 86% (Figure 12) due to the increment of HCl flux through the membrane (1.06-1.26 kg h^{-1}·m^{-2}).
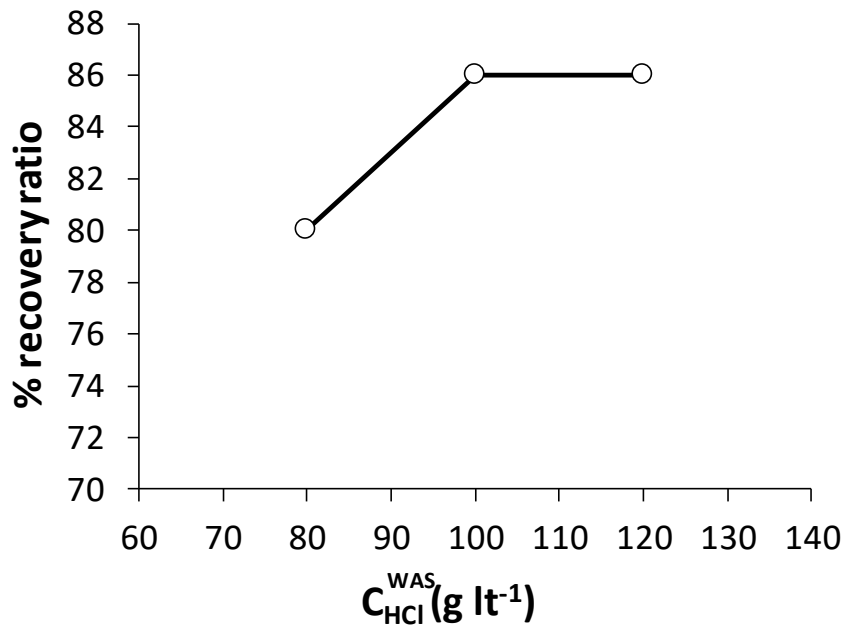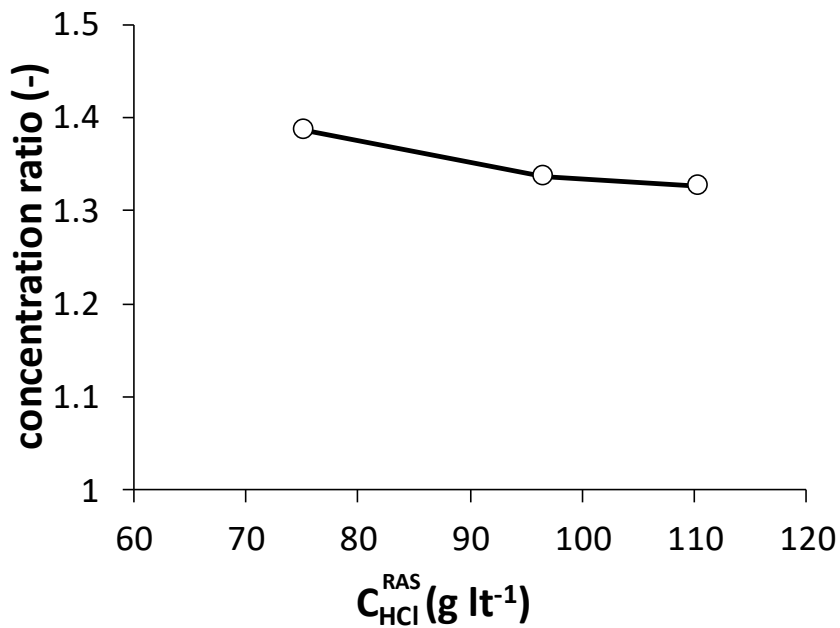

Figure 12. Recovery ratio as a function of C_{HCl}^{WAS}.

For what concern the Membrane Distillation unit, the concentration ratio *CR* is defined by:

$$CR = \frac{C_{HCl}^{RPS}}{C_{HCl}^{RAS}} \tag{34}$$

which is the hydrochloric acid mass concentration ratio in the *Recovered Pickling Solution* C_{HCl}^{RPS} and in the *Recovered Acid Solution* C_{HCl}^{RAS}. According to the Figure 13, the higher the C_{HCl}^{RAS}, the lower the concentration ratio *CR*. In fact, the increase of C_{HCl}^{RAS} causes a reduction of the water flux and an increasing of the HCl flux through the MD membrane.

Figure 13. Concentration ratio as a function of C_{HCl}^{RAS}.

Due to the change of operating conditions, also the membrane area requirements in the DD and MD units changed, as reported in Fig. 14 *versus* the optimal C_{HCl}^{WAS}. In particular, MD and DD membrane area increases as C_{HCl}^{WAS} increases. In fact, the higher C_{HCl}^{WAS}, the higher is the quantity of acid to be recovered through the DD membrane, which leads to an increase in membrane area requirement. Moreover, also the *WAS* flow rate increases, thus increasing the DD *Draw Solution* flow rate required. This leads to an increase in the amount of water to be transferred in the MD unit from the feed to the permeate side, allowed by an increase in the membrane area available.
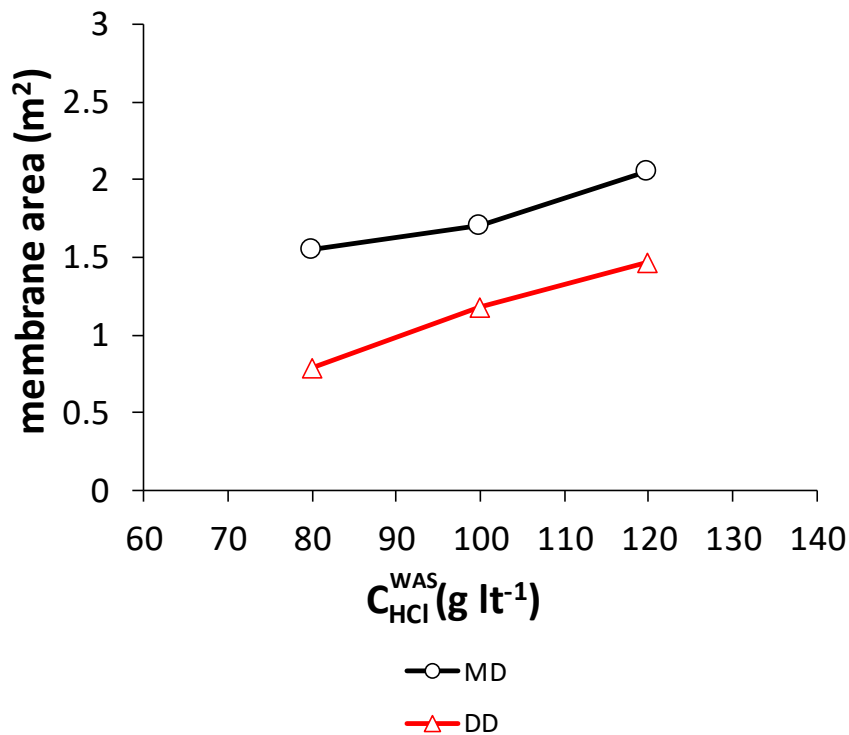
Figure 14. Membrane area variation in DD and in MD units as a function of C_{HCl}^{WAS}.

4.4 Reactive precipitation and Brine MD stages

In the final step of the process, which is the reactive precipitation of iron hydroxide from the metals rich brine, the oxidant and alkaline reactants volumetric flow rates are correlated to the iron content in the inlet stream. The amount of Fe to be precipitated in the reactor has to close the overall mass balance of the process. Since the Fe release in the pickling process is proportional to the manufactured steel flowrate, this can be considered constant. However, to due the lower Fe concentration in the pickling bath, a lower amount of Fe will be removed by the entrainment outlet stream, which leads to a slight increase in the *Metals Sludge* flow rate (see Table 4) and the relevant mass flow rate of iron to be precipitated (1.68-1.71 kg/h). As a consequence, slightly higher reagents consumptions are registered, more evident for alkaline reactant, due to the larger amount of acid to be neutralised before precipitation.

Table 4. Main streams properties as a function of C_{HCl}^{WAS} in the reactive precipitation stage (pH of the outlet stream = 4, drag solution in MS = 35%)

	C_{HCl}^{WAS} (g l^{-1})		
	80	100	120
Metal sludge flow rate (kg h^{-1})	10.6	11.2	12.0
C_{HCl}^{MRB} (g l^{-1})	15.6	14.1	17.8
C_{Fe}^{MRB} (g l^{-1})	125	112	101
Oxidizing reactant (l h^{-1})	3.15	3.18	3.20
Alkaline reactant (l h^{-1})	4.40	4.44	4.63

Concerning the Brine Membrane Distillation unit, as shown in Table 5, the *Outlet Reactive Precipitator* volume flow rate increases (13.0-15.4 l h^{-1}) as the *Metals Rich Brine* flow rate increases. On the other hand, NH$_4$Cl concentration decreases (181-160 g l^{-1}) due to a dilution effect for the *MRB* flow rate increment. As expected, Brine MD outlet streams (*Fluxing solution* and *Distillate*) flow rates raise as the *Outlet Reactive Precipitator* stream increases. The values reported in Table 5 are calculated by imposing the maximum allowable ammonium chloride concentration of 350 g l^{-1}, as stated above.

In addition, the *Distillate* stream recovered from the Brine MD, reaching a value around 7 l h^{-1}, can contribute for the 70% to the process water stream required in the Demo.

Table 5. Main streams flow rates as a function of C_{HCl}^{WAS} in the Brine-MD

Outlet Reactive Precipitator	C_{HCl}^{WAS} (g l^{-1})		
	80	100	120
F (l h^{-1})	13.0	14.1	15.4
$C_{NH4Cl,waste}$ (g l^{-1})	181	168	160
Fluxing Solution	C_{HCl}^{WAS} (g l^{-1})		
	80	100	120
F (l h^{-1})	6.72	6.77	7.06
$C_{NH4Cl,waste}$ (g l^{-1})	350	350	350
Distillate	C_{HCl}^{WAS} (g l^{-1})		
	80	100	120
F (l h^{-1})	6.14	7.22	8.23
$C_{NH4Cl,waste}$ (g l^{-1})	0	0	0
	C_{HCl}^{WAS} (g l^{-1})		
Membrane Area (m^2)	2.03	2.43	2.74

5. Conclusions

This work focuses on a novel approach for the optimal regeneration 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). A purposely-developed simulation tool is presented along with its application for the design and operational sensitivity analysis of a demonstration pilot plant to be installed as a final outcome of the EU-funded ReWaCEM project (www.rewacem.eu).

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 process simulator. The parametric analysis shows the effect of increasing the optimal hydrochloric acid concentration in the *Waste Acid Solution* on the main process streams. 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%). Moreover, the acid solution concentration step is effectively achieved in the MD unit, where HCl is increased until acid flux through the microporous membrane reaches values around the 13.1-14.6% of the recovered acid recirculated to the pickling tank. This allows the operation of the integrated system under optimal conditions for the pickling baths by continuously controlling the concentration of free acid and iron in the pickling solutions.

A final reactive precipitation stage allows the neutralisation of the metal rich waste. Here, pure iron hydroxide is obtained as by-product and the remained solution is sent to a final MD unit where it is concentrated to be reused in the fluxing baths of the hot-dip galvanizing plant. In this way, a further integration of the whole process with savings in chemicals and process water is obtained. Successful operation of the integrated process will allow to avoid the standard periodic steps of withdrawing and refilling pickling baths, which constitute one of the major environmental and economic drawbacks of the process. At the same time, this guarantees the pickling operation under optimal conditions, thus reducing pickling time and enhancing the overall system effectiveness.

Acknowledgments

Acronyms

AEM	Anion Exchange Membrane
CSTR	Continuous-flow Stirring Tank Reactor
DD	Diffusion Dialysis
DS	Draw Solution
FS	Fluxing Solution
MD	Membrane Distillation
MRB	Metals Rich Brine
MS	Metals Sludge
MU	Make-up
ORP	Outlet Reactive Precipitator
PFD	Process Flow Diagram
PW	Process Water
RAS	Recovered Acid Solution
RPS	Recovered Pickling Solution
WAS	Waste Acid Solution

Nomenclature

A (m^2)	membrane area
C (g l^{-1})	mass concentration
F (l h^{-1})	volumetric flow rate
J (kg h^{-1} m^{-2})	mass flux
k (kg ton^{-1})	kinetic constant
MM (g mol^{-1})	molar mass
P (m h^{-1})	membrane permeability
pH	pH value
R (l bar K^{-1} mol^{-1})	gas constant
RR	recovery ratio
T (K)	temperature
U_{salt} (m h^{-1})	acid permeability due to the iron salt
w (kg h^{-1})	mass flow rate

Greek letters

α	drag solution percentage
Δ	difference of value
ρ (kg m^{-3})	mass density

Superscripts

alk	alkaline
av	average value
D	diffusion dialysis diffusate stream
Dist	distillate
DD	diffusion dialysis
DS	draw solution stream
entr, in	entrainment stream, inlet
entr, out	entrainment stream, outlet
evap	evaporating stream
FS	fluxing solution
in	inlet
MRB	metals rich brine stream
MS	metals sludge
MU	make-up stream
ORP	outlet reactive precipitator
Ox	oxidant
out	outlet
Perm	permeate
pw	process water stream
R	diffusion dialysis retentate stream
RAS	recovered acid solution stream
RPS	recovered pickling solution stream
WAS	waste acid solution stream

Subscripts

d	diffusate stream of the DD unit
drag	water molecules dragged by the acid through the membrane in DD
evap	evaporated stream
i	component i
in	inlet
min_{r-d}	minimum concentration difference between retentate and diffusate of the DD unit
mol	molar concentrations
os	osmotic flux
r	retentate stream of the DD unit
s	steel manufactured
tot	entire stream
w	water

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