

# Metals recovery from waste pickling solutions by reactive precipitation

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Pickling is one of the most important steps in steel manufacturing industry. During the process, an acid reacts to dissolve surface oxides, thus metals ions are accumulated in the pickling solution. Waste acid disposal is a critical issue for the hot-dip galvanizing industry in terms of environmental damage and high costs. For this reason, a continuous regeneration of industrial pickling solutions and recovery of valuable materials was proposed, by integrating cutting-edge membrane technologies applied to the case of a HCl-based pickling process for the treatment of carbon steel. The aim is to recover the HCl and, besides that, to recover metal ions (mainly Fe and Zn) by reactive precipitation. In this way, waste streams minimization and the use of a circular approach lead to an environmental and economic sustainable process within the hot-dip galvanizing industry. Reactive precipitation process reliability was proved through lab-scale experiments, in order to collect information for the design of a pilot-plant to be installed in the real industrial environment of Tecnozincò SrL (Carini, Italy) hot-dip galvanizing plant. Experiments were conducted in a continuous stirred tank reactor by feeding in parallel the acidic metals-rich feed, an alkaline reactant and an oxidant. Quantities of Fe and Zn were detected in the outlet solution and in the precipitate to evaluate the recovery efficiency and the process selectivity. Some key parameters, such as temperature and pH, were studied by varying inlet streams flow rates. A very effective metals separation was obtained, with Fe(III) hydroxide solids at a purity of 99 %. Zn ions were successfully kept in solution to generate a zinc/ammonium chloride-rich stream, to be reused in the fluxing baths of the hot-dip galvanizing plant.

## 1. Introduction

The pickling process is one of the most important steps in the hot-dip galvanizing process as it allows the complete removal of oxidized layers from the surface of manufactured steel pieces. In fact, the quality of the covering zinc layer during the immersion of manufactured steel in the molten zinc bath strongly depends on the efficiency of the pickling step, as it is essential to have a good uniform contact surface. In the pickling acid bath, typically HCl attacks metal oxides on the surface, dissolving them. Thus, FeCl<sub>2</sub> is produced during the pickling treatment, reaching Fe<sup>2+</sup> concentrations up to 200-250 g/L, while the acid concentration decreases from values above 100 g/L to values below 20 g/L. At these latter conditions, a pickling bath is considered spent (Regel-Rosocka, 2010), due to the very low pickling rate, and its replacing is necessary. As pickled goods and hooks are commonly covered with zinc, also an accumulation of Zn<sup>2+</sup> during the pickling process can be observed, thus making the pickling solution even more ineffective (Regel et al., 2001). Thus, a more efficient pickling process could be very crucial to achieve a sustainable development of hot-dip galvanizing industry (Kong and White, 2010). With the perspective of a circular approach, beside the acid recovery, successfully obtained in a Diffusion Dialysis step (Gueccia et al., 2019; Gueccia et al., 2020), also the recovery of the heavy metals present in pickling solutions should be taken in consideration. In fact, the innovative system proposed in a previous authors' paper aims at: (i) continuous regenerating the pickling solutions, thus enhancing the pickling rate and process performance; (ii) recovering valuable compounds (e.g. acid and metals); and (iii) reducing industrial waste

disposal (Culcasi et al., 2019). For this purpose, a process simulator was developed to predict the integrated process operation and design the pilot-plant (Gueccia et al., 2021).

Several technologies, such as solvent extraction (Regel et al., 2001) and ion-exchange resins (Marañón et al., 2000) can be used to separate metals, but they suffer from large energy and chemicals consumptions and significant investment and operating costs (Kerney, 1994). Also pyrohydrolysis is widely applied for the treatment of waste pickling solutions, providing acceptable recovery of Fe as  $\text{Fe}_2\text{O}_3$  (Devi et al., 2014), but only at the large industrial scale. Liquid-liquid extraction has been also studied to extract Zn from pickling solution (Randazzo et al., 2019). However, for the treatment of pickling waste solutions in small/medium-size plants and aiming at the continuous recovery of metals, reactive precipitation was selected as the more feasible technology to be included in the innovative integrated process.

Several alkaline reactants have been analysed and ammonium hydroxide was selected, though not being the most cost-effective and environmental advantageous option, as it allows to obtain as a by-product a zinc/ammonium chloride solution, which can be used in the fluxing baths of the hot-dip galvanizing plant. With this purpose,  $\text{Fe}^{3+}$  was precipitated and recovered as hydroxide, while Zn was kept in the solution. Two important aspects have to be monitored to achieve this goal: (i) ensure that  $\text{Fe}^{2+}$  is totally oxidized to  $\text{Fe}^{3+}$ ; (ii) keep the pH at an intermediate value between Fe and Zn hydroxides precipitation.

$\text{Fe}(\text{OH})_3$  precipitation pH is in the range of 2-3, while  $\text{Zn}(\text{OH})_2$  precipitates in the range 6-7. Therefore, to accomplish the metals fractionated precipitation, hydrogen peroxide and ammonia hydroxide are fed in order to oxidize  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  and to precipitate iron hydroxide maintaining a pH of 4. The precipitated iron hydroxide is separated from the slurry via filtration and the filtered solution can be reused in the fluxing bath, while the separated solid particles of  $\text{Fe}(\text{OH})_3$  can be dried and sold to the market (e.g. in painting industry or in wastewater treatment plants (Zhao et al., 2015).

Furthermore, this option allows to overcome the limit of neutralisation with traditional hydroxides (e.g. NaOH or  $\text{Ca}(\text{OH})_2$ ) leading to the co-precipitation of different metals, which can dramatically affect the purity of precipitates (Agrawal and Sahu, 2009).

In the present work, a lab-scale Continuous Stirred Tank Reactor (CSTR) was used to assess the feasibility of the reactive precipitation process to separate Fe from Zn by recovering two valuable pure products and to collect valuable information for the optimal design of equipment and operation of the reactive precipitation section of the pilot-plant.

## 2. Experimental

### 2.1 Materials and methods

Experiments were carried out with artificial solutions prepared using 37 % hydrochloric acid (Sigma Aldrich), Fe(II) chloride tetrahydrate (Carlo Erba,  $\geq 99\%$ ), Zn chloride (Carlo Erba,  $\geq 99\%$ ) and deionized water, generated by a two-stage reverse osmosis unit (conductivity below  $5\ \mu\text{S}/\text{cm}$ ). The composition of the investigated solution was of 20, 123 and 10 g/L of HCl, Fe(II), and Zn, respectively. These values represent the predicted concentrations of feed stream reaching the reactive precipitation unit in the pilot plant, as foreseen by predictive simulations (Culcasi et al., 2019).

$\text{NH}_4\text{OH}$  commercial concentrated solution (28-30 % w/w) and concentrated  $\text{H}_2\text{O}_2$  (30 % w/w, or rather 9.7 M) were used as alkaline and oxidant reactants, respectively.

The acid concentration was detected by titration with  $\text{Na}_2\text{CO}_3$  solutions.  $\text{Fe}^{2+}$  ions concentration was measured by spectrophotometry (spectrophotometer Beckman DU 800), by adding 1,10-phenanthroline ((Sigma Aldrich,  $\geq 99\%$ ) and characterizing the samples at a wave length of 510 nm.  $\text{Fe}^{3+}$  ions concentration was determined by subtracting  $\text{Fe}^{2+}$  to the total iron concentration. To evaluate total iron concentration, hydroxylammonium chloride (Chem-lab,  $\geq 99\%$ ) was added to reduce all iron ions to  $\text{Fe}^{2+}$  and then it was analysed as already described. Zn concentration was detected by atomic absorption (Shimadzu mod. AA6200).

### 2.2 Experimental set-up and procedure

Experiments were carried out in a purposely-developed laboratory set-up where the reactive precipitation occurred in a continuous stirred tank reactor (CSTR, Figure 1). The reactor capacity is 1 L, with an internal and external diameter of 8 and 9 cm, respectively, and a height of 26.6 cm. A marine propeller (diameter of 6 cm) was selected and designed to achieve the best mixing in the reactor.

Since the oxidation reaction was exothermic, and the high temperature could affect the precipitate product (Markov. et al., 1990), the CSTR was immersed in a cooling bath (i.e. ice and water) to keep the temperature below  $50^\circ\text{C}$ . The temperature value was selected to ensure no modification of the iron hydroxide structure.

Four peristaltic pumps (Kronos KRFM-10) were employed in the set-up, three for the inlet streams and one for the continuous draining of the CSTR.

The startup procedure involved an initial filling step with the acidic feed. Then, hydrogen peroxide was injected to initiate the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  and, lastly, injection of ammonium hydroxide solution started. Propeller speed was set at 700 rpm. When the desired volume value for the specific test was reached, the outlet pump was set to a suitable flow rate which ensures no volume variation in the reactor tank. After that, a period equal to the residence time ( $\tau$ ) was waited, considering this the starting point of the experiment.

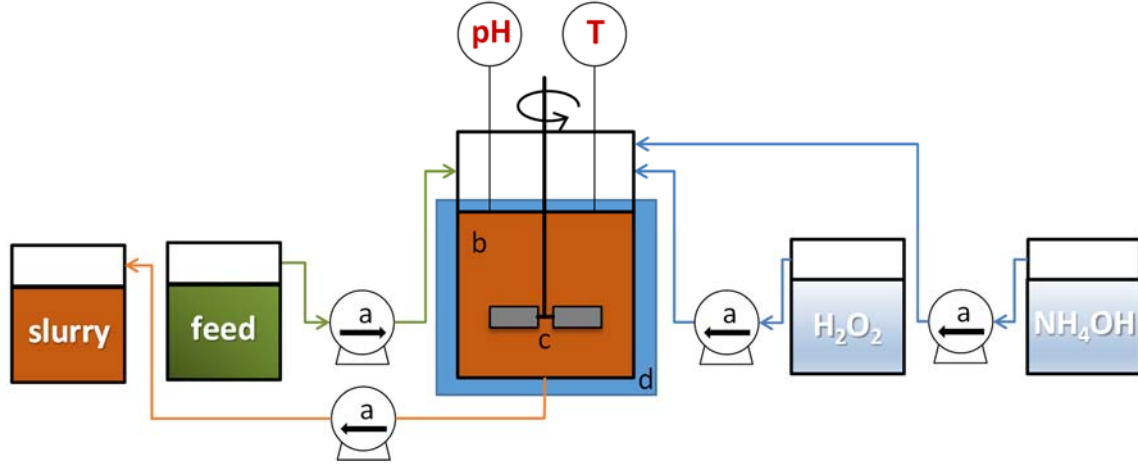


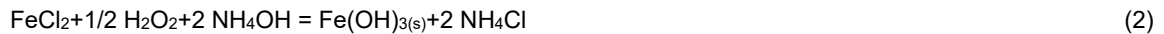
Figure 1: Experimental set-up for continuous reactive precipitation test: (a) pumps, (b) CSTR, (c) marine propeller, (d) cooling bath.

Operating conditions set during the experiments are summarized in Table 1.

Table 1: Operating conditions for the oxidation-precipitation process test

Operating parameter	
Acidic metals-rich feed flow rate (mL/min)	9
Alkaline reactant flow rate (mL/min)	3.2-3.5
Oxidant reactant flow rate (mL/min)	2
Reactor capacity (L)	1
Propeller speed (rpm)	700
pH	4
Temperature ( $^{\circ}\text{C}$ )	< 50

The flow rates of the inlet reactants were estimated considering that the following reactions occur in such conditions (Hardwik, 1957):



During each experiment, pH and temperature were constantly monitored by a pH-meter (Hanna Instruments) and a thermometer. Experiments duration spanned from  $6\tau$  to  $8\tau$  and samples were withdrawn at intervals of  $2\tau$ . Samples were filtered by a vacuum pump and both solids and filtered solution were analyzed. Total Fe concentration was detected in the solution to evaluate the process recovery efficiency, whereas Fe speciation ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) was considered in the solid to estimate the efficiency of the oxidation during the process. To evaluate the purity of the final product, also Zn was detected in the last solid sample. For this purpose, the precipitate was washed with deionized water and dried in an oven for 48 h at  $70^{\circ}\text{C}$ . Then, it was washed with an HCl 1 M solution (using stoichiometric quantities plus 10 % excess) to dissolve the metals and allow their detection in a liquid solution.

The selectivity of fractionated precipitation depends on the effectiveness of both the oxidation and of the precipitation processes, thus some parameters, such as the Recovery Efficiency and the  $\text{Fe}(\text{OH})_3$  purity, were used to assess the CSTR performance, as defined according to the following equations:

$$\text{Recovery Efficiency (\%)} = \frac{c_{Fe}^{in} - c_{Fe}^{sol}}{c_{Fe}^{in}} \times 100 \quad (3)$$

where  $c_{Fe}^{in}$  and  $c_{Fe}^{sol}$  represent the total Fe concentration in the inlet feed and in the sampled filtered solution, respectively.

$$\text{Fe(OH)}_3 \text{ purity (\%)} = \frac{m_{Fe}}{m_{Fe} + m_{Zn}} \times 100 \quad (4)$$

where  $m_{Fe}$  and  $m_{Zn}$  are the (ponderal) amounts of Fe and Zn detected in the solid sample, respectively.

### 3. Results and discussion

In order to assess the performance of the process, an experimental test was carried out by setting a residence time of 27 minute, mimicking the actual residence time in a pilot reactor capacity of 1 L. The initial flow rates of the acidic metals-rich feed,  $H_2O_2$  and  $NH_4OH$  were set at 9, 2 and 3.2 mL/min, respectively (calculated according to the reactor capacity scale factor). In particular, excess factors of 2 and 1.1, compared to the stoichiometric values, were used for  $H_2O_2$  and  $NH_4OH$  flow rates, respectively, as starting values.

In Figure 2, values of key process parameters are reported as a function of the normalised reaction time. As shown, a good process stability was obtained. In fact, pH (Figure 2a) and temperature (Figure 2b) are stable and always below the thresholds values of 4 and 50 °C, respectively.

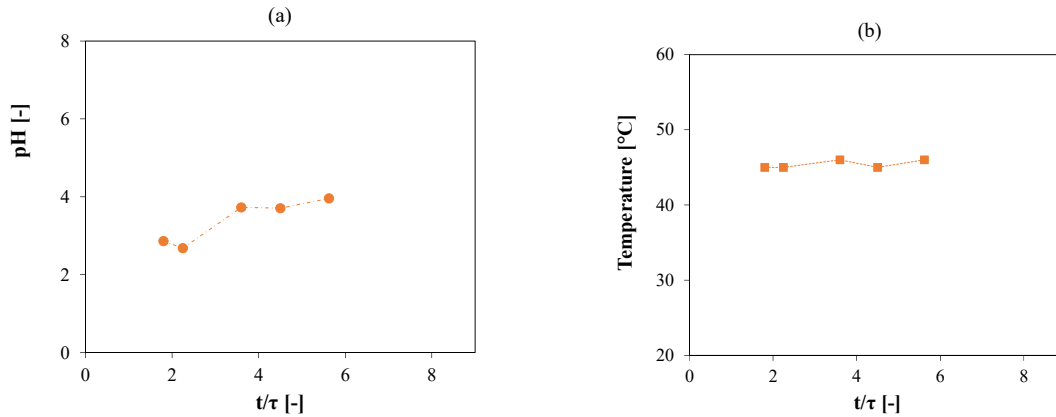


Figure 2: (a) pH and (b) temperature values vs the normalised reaction time. Feed solution: 20 g/L HCl, 123 g/L  $Fe^{2+}$ , 10 g/L Zn;  $H_2O_2$  30 % w/w and  $NH_4OH$  28-30 % w/w. Feed,  $H_2O_2$  and  $NH_4OH$  flow rates: 9, 2 and 3.2-3.5 mL/min. Volume: 1 L.

For what concern the pH, starting from a value of 3.2 mL/min, a pH of about 3 was achieved, thus the flow rate was increased to the higher value of 3.5 mL/min and a good control of the parameter was achieved. Conversely, regarding the oxidant stream, the flow rate value of 2 mL/min was confirmed. Thus, these operating conditions were selected for the tuning of the process simulator. Regarding the temperature, as shown in Figure 2b, this parameter was kept at an almost constant value of 45 °C.

With respect to the process performance parameters, very high values of Recovery Efficiency were obtained during the test, namely always higher than 99.9 %. In particular, such low amounts of iron in solution were detected only in the first sample, while no iron was found in all other samples, thus indicating a 100 % recovery.  $Fe^{2+}$  and  $Fe^{3+}$  concentrations were detected in the precipitate and results are presented in Figure 3. As shown,  $Fe^{3+}$  amount, compared to the total Fe, was very high since the beginning with values above 90 %.

Purity of the final  $Fe(OH)_3$  solid product was evaluated by detecting Fe and Zn contents. A very high value of 99 % was achieved, thus demonstrating the good efficiency of the process.

The result of the absence of Fe in solution coupled with the very high values of  $Fe^{3+}$  (compared to  $Fe^{2+}$  and to Zn) in the solid implies a good efficiency of the overall process, where oxidation and precipitation reactions coexist, as the iron is continuously removed from the solution in the form of highly pure  $Fe(OH)_3$  solid product.

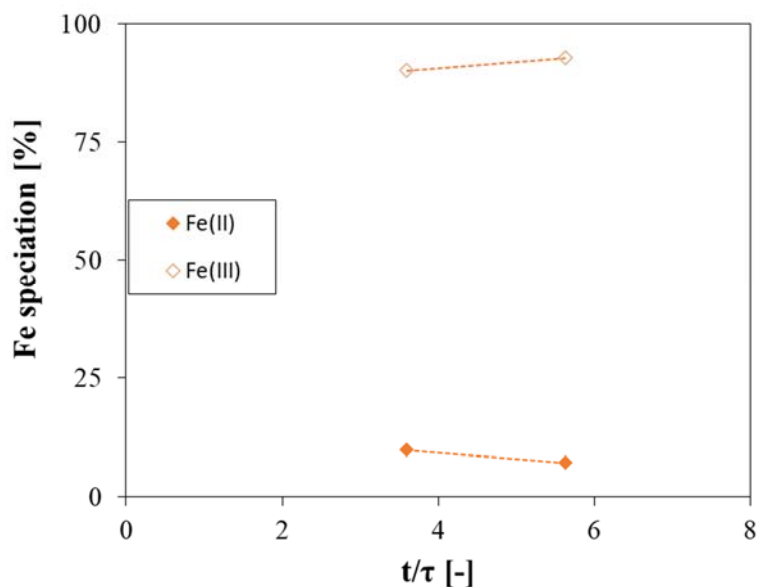


Figure 3: Fe speciation ( $Fe^{2+}$  and  $Fe^{3+}$ ) in the precipitated solid vs the normalized reaction time. Feed solution: 20 g/L HCl, 123 g/L  $Fe^{2+}$ , 10 g/L Zn;  $H_2O_2$  30 % w/w and  $NH_4OH$  28-30 % w/w. Feed,  $H_2O_2$  and  $NH_4OH$  flow rates: 9, 2 and 3.2-3.5 mL/min. Volume: 1L

#### 4. Conclusions

A lab-scale Continuous Stirred Tank Reactor (CSTR) was used to assess the feasibility of reactive precipitation to fractionally separate Fe and Zn from a spent pickling solution. This experimental campaign was propaedeutical to the design of a pilot-plant to be installed in the real industrial environment of the Tecnozinco Srl (Carini, Italy) hot-dip galvanizing plant. In fact, the integrated process proposed for minimizing waste streams generation and using of a circular approach, includes cutting-edge membrane technologies, to recover the HCl, and reactive precipitation, to recover metal ions. In this way, valuable materials are recovered from the pickling process, leading to an environmental and economic sustainable process within hot-dip galvanizing industry.

Separation of the heavy metals, at high concentrations, was successfully achieved. As  $Fe^{3+}$  and  $Zn^{2+}$  show very different precipitation pH, a  $Fe^{2+}/Fe^{3+}$  oxidation step was necessary. For this purpose, hydrogen peroxide (30 %w/w) was used. Moreover, to obtain as a by-product a zinc/ammonium chloride solution to be re-used in the fluxing baths, ammonium hydroxide (28-30 %w/w) was selected as alkaline reactant for the precipitation process. Flow rates of the acidic metals-rich feed, alkaline reactant and oxidant were tuned to better achieve the optimal operating conditions of pH and temperature during the process with a reactor capacity of 1L.

All the evaluated process parameters showed that an efficient reactive precipitation process both in terms of process feasibility and precipitate purity can be obtained. In fact, no iron was detected in the solution filtered from the slurry samples (Recovery Efficiency of 99.9 %) and a highly pure Fe(III) hydroxide product (99 % purity) was obtained.

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