CHEMICAL ENGINEERING TRANSACTIONS

VOL. 86, 2021

A publication of AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš

**ISBN** 978-88-95608-84-6; **ISSN** 2283-9216

DOI: 10.3303/CET2186175

# Metals Recovery from Waste Pickling Solutions by Reactive Precipitation

Serena Randazzo*, Daniele La Corte, Rosa Gueccia, Andrea Cipollina, Giorgio Micale

Dipartimento di Ingegneria, Università degli studi di Palermo, Palermo, 90128, Italy
serena.randazzo@unipa.it

Pickling is one of the most important steps in steel manufacturing industry. During the process, an acid reacts with the surface oxides causing metal ions accumulation in the pickling solution. Disposal of the waste acid represents a critical issue for the hot-dip galvanizing industry in terms of environmental damage and high costs. Recovering of the main products by using an integrated process, with the perspective of a circular approach, could minimize the wastewater production, leading to reinvigorate this industrial sector economy. In this context, recovery of the metal ions mainly present in the pickling solution, such as Fe and Zn, becomes a critical issue.

In this work, the 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 Tecnozinco SrL (Carini, Italy) hot-dip galvanizing plant. Experiments were carried out in a continuous stirred tank reactor by feeding the acidic metals-rich stream, an alkaline reactant and an oxidant. The quantity of Fe in the outlet solution and its speciation in the precipitate were detected to evaluate the recovery efficiency and the process quality, whereas Zn concentration in the precipitated was detected for determining the product purity. Some key parameters, such as temperature and pH, were studied by varying inlet streams flow rates. A very effective metals separation was observed by obtaining Fe(III) hydroxide at a high purity of 99 %. Zn ions were successfully separated by keeping them in solution with the aim of generating a zinc/ammonium chloride 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 and uniform contact surface. In the pickling bath, the acid, typically HCl, reacts with metal oxides dissolving them in the solution. Thus, $FeCl_2$ is produced and $Fe^{2+}$ concentrations up to 200-250 g/L can be reached, whereas the concentration of the acid is reduced from values above 100 g/L to below 20 g/L. At this condition, a pickling bath is considered spent (Regel-Rosocka, 2010) because of the poor pickling rate, and its replacing is necessary. As pickled goods and hooks are commonly covered with zinc, also an accumulation of $Zn^{2+}$ ions can be observed, thus making the pickling solution even more ineffective (Regel et al., 2001).

Thus, an improvement of the pickling process, with the aim of a sustainable development, could benefits the 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 unit (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 pilot-plant installed at the Tecnozinco SrL (Carini, Italy) hot-dip galvanizing plant, which design and testing have been reported in previous authors' papers (Culcasi et al., 2019; Gueccia at al., 2021), includes both the membrane technologies, to recover the acid, and the reactive precipitation, to recover the metals. The novelty of this innovative system proposed lies

Paper Received: 13 October 2020; Revised: 5 March 2021; Accepted: 21 April 2021
Please cite this article as: Randazzo S., La Corte D., Gueccia R., Cipollina A., Micale G., 2021, Metals Recovery from Waste Pickling Solutions by Reactive Precipitation, Chemical Engineering Transactions, 86, 1045-1050 DOI:10.3303/CET2186175

in the possibility of performing the pickling process by continuous regenerating the solution leading to reduce industrial waste disposal and recovering valuable compounds (e.g. acid and metals).

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 $Fe_2O_3$ (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. Although it is not affordable and environmental advantageous, this base leads to the production of a zinc/ammonium chloride solution as a by-product, which can be adopted in the fluxing baths of the hot-dip galvanizing plant. With this purpose, $Fe^{3+}$ has to be precipitated and recovered as hydroxide, while Zn should be kept in the solution. Two important aspects have to be monitored to achieve these goals: (i) ensuring that all $Fe^{2+}$ ions are oxidized to $Fe^{3+}$; (ii) keeping the pH at an intermediate value between the ones of Fe and Zn hydroxides precipitation.

As $Fe(OH)_3$ precipitation pH is in the range of 2-3, while $Zn(OH)_2$ precipitates at a pH of 6-7, hydrogen peroxide and ammonium hydroxide could be introduced with the aim of oxidizing $Fe^{2+}$ to $Fe^{3+}$ and of precipitating Fe(III) hydroxide maintaining a pH of 4. In this way, it is possible to obtain an effective separation of the two metals. The separated solid particles of $Fe(OH)_3$, with an expected micrometric size, can be recovered from the slurry by filtration and, after drying, can be sold to the market (e.g. in painting industry or in wastewater treatment plants (Zhao et al., 2015).

It's worth noting that this process option also allows to overcome the limit of the traditional neutralisation process by using hydroxides (e.g. NaOH or $Ca(OH)_2$), where co-precipitation of different metals occur and purity of precipitates is compromised (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, ≥ 99 %), Zn chloride (Carlo Erba, ≥ 99 %) and deionized water (conductivity below 5 $\mu$S/cm). The composition of the investigated solution was 20, 123 and 10 g/L of HCl, Fe(II), and Zn, respectively. These values represent the predicted concentrations of the feed stream reaching the reactive precipitation unit in the pilot-plant (Culcasi et al., 2019).

$NH_4OH$ commercial concentrated solution (28-30 % w/w) and concentrated $H_2O_2$ (30 % w/w, or rather 9.7 M) were used as alkaline and oxidant reactants, respectively.

The acid concentration was detected by titration with $Na_2CO_3$ solutions. $Fe^{2+}$ ions concentration was measured by spectrophotometry (spectrophotometer Beckham DU 800), by adding 1,10-phenanthroline ((Sigma Aldrich, ≥ 99%) and characterizing the samples at a wave length of 510 nm. $Fe^{3+}$ ions concentration was determined by subtracting $Fe^{2+}$ to the total iron concentration. To evaluate total iron concentration, hydroxylammonium chloride (Chem-lab, ≥ 99%) was added to reduce all iron ions to $Fe^{2+}$ 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 was 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.

As 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°C. This 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 from CSTR.

The start-up procedure involved an initial filling step with the acidic feed. Then, hydrogen peroxide entered to initiate the oxidation of $Fe^{2+}$ to $Fe^{3+}$ and, lastly, injection of ammonium hydroxide solution started. Propeller speed was set at 700 rpm. When 1 L volume had been reached, the outlet pump was switched on. Then, after the residence time ($\tau$), the experiments started.

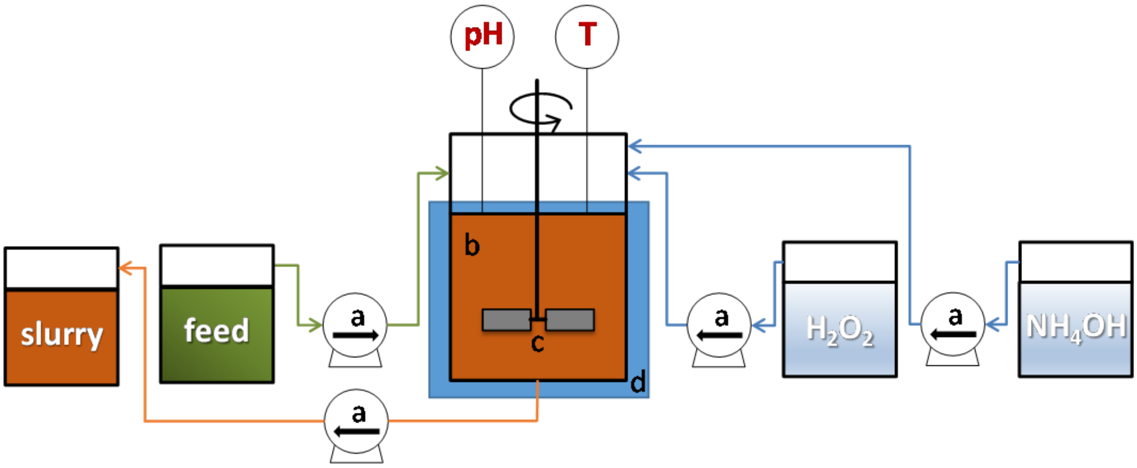

*Figure 1: Experimental set-up for continuous reactive precipitation test: (a) pumps, (b) CSTR, (c) marine propeller, (d) cooling bath.*

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 (°C) | < 50 |

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

$$HCl + NH_4OH = NH_4Cl + H_2O \quad (1)$$

$$FeCl_2+1/2\ H_2O_2+2\ NH_4OH = Fe(OH)_{3(s)}+2\ NH_4Cl \quad (2)$$

The values of 9, 3.2 and 2 mL/min, reported inn Table 1 for the acidic metals-rich feed, $NH_4OH$ and $H_2O_2$ respectively, were calculated according to the real reactor capacity scale factor. In particular, excess factors of 1.1 and 2, compared to the stoichiometric values, were used for $NH_4OH$ and $H_2O_2$ flow rates estimation as starting points.

During the experiments, pH and temperature were constantly monitored by a pH-meter (Hanna Instruments) and a thermometer. Experiments lasted about 6 $\tau$ and samples were withdrawn at intervals of 2 $\tau$. Then, they 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 (eq. 3), whereas Fe speciation ($Fe^{2+}$and $Fe^{3+}$) was considered in the solid to estimate the effectiveness of the oxidation during the process. For this purpose, the precipitate was washed with deionized water and dried in an oven for 48 h at 70 °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. Moreover, to evaluate the purity of the final product (eq. 4), also Zn was detected in the last solid sample.

The recovery efficiency and the $Fe(OH)_3$ purity, were used to assess the CSTR performance, as defined according to the following equations:

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

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

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

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, a test was carried out accomplishing the operative conditions reported in Table 1 and by setting a residence time of 67 minute, mimicking the actual residence time in a pilot reactor capacity of 1 L.

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.

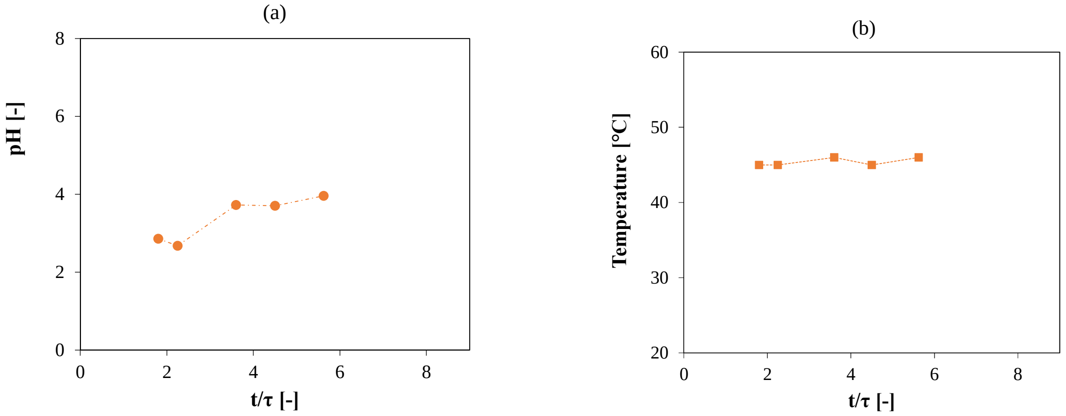

*Figure 2: (a) pH and (b) temperature values vs the normalised reaction time. Feed solution: 20 g/L HCl, 123 g/L $Fe^{2+}$, 10 g/L Zn; $H_2O_2$ 30 % w/w and $NH_4OH$ 28-30 % w/w. Feed, $H_2O_2$ and $NH_4OH$ flow rates: 9, 2 and 3.2-3.5 mL/min. Volume: 1 L.*

For what concerns 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 %, as very low amounts of Fe were detected in the solution. In particular, it was revealed only in the first sample, while no Fe was found in all other samples, thus indicating a 100 % recovery.

Moreover, $Fe^{2+}$ and $Fe^{3+}$ concentrations were detected in the precipitates recovered from the slurry-samples 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.

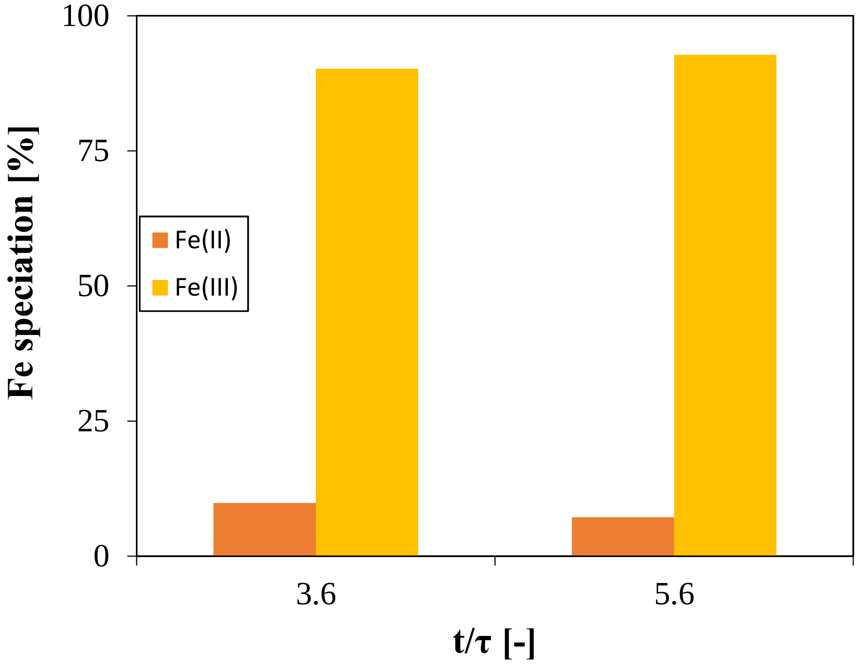

*Figure 3: Fe speciation ($Fe^{2+}$ and $Fe^{3+}$) in the precipitated solid vs the normalized reaction time. Feed solution: 20 g/L HCl, 123 g/L $Fe^{2+}$, 10 g/L Zn; $H_2O_2$ 30 % w/w and $NH_4OH$ 28-30 % w/w. Feed, $H_2O_2$ and $NH_4OH$ flow rates: 9, 2 and 3.2-3.5 mL/min. Volume: 1L*

## 4. Conclusions

A lab-scale CSTR has been used to assess the feasibility of reactive precipitation to fractionally separate Fe and Zn from pickling solutions. This experimental campaign was preparatory to the design of a pilot-plant to be installed in the Tecnozinco SrL (Carini, Italy) hot-dip galvanizing plant, where a unit of reactive precipitation is included with the aim of recovering the metal ions. In fact, the goal of the innovative integrated process proposed is to minimize waste streams generation and use a circular approach, by also recovering valuable materials, 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 can be obtained in terms of process feasibility and precipitate purity. 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.

## Acknowledgments

This work was supported by the EU within ReWaCEM project (Resource recovery from industrial Wastewater by Cutting Edge Membrane technologies, Horizon 2020 program [grant number. 723729].

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