# ZINC ELECTROWINNING FROM GALVANIZED MILD STEEL SCRAPS

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## Abstract

Industrial uses of zinc consist essentially of producing galvanized steel. From mining to production of pure metal, numerous operations and unit processes are used. The main source of that metal is sphalerite ((Zn,Fe)S) from which the zinc is extracted by different methods (i.e., roasting followed by acid leaching, pressure leaching, and, more recently, by bioleaching). For involving less processing steps one third of pure metallic zinc production comes from recycling of secondary sources indicating a trend to be followed. Thus, the adoption of alternative practices, such as the recovery of galvanized steel scraps, stimulates the development of urban mining and sustainable use of non-renewable mineral resources. Besides that, the Zinc industry is also worried about reducing energy cost related to the electrowinning process. This work, therefore, presents a study of the best condition found for the leaching stage considering amphoteric characteristics of zinc and an electrowinning study based on current efficiency and specific energy consumption.

**Keywords**: zinc, zinc recovery, galvanized steel, electrowinning.

## 1. INTRODUCTION

Zinc is a blue-white metal that dissolves in acids and bases[1]. In contact with dilute sulphuric acid solution, it presents in the cationic form of Zn2+; however, in contact with solutions of alkaline hydroxides (*i.e.*, NaOH) presents in the anionic form of zincate ($ZnO_2^{2-}$)[2,3]. It is because of this ability to dissolve in acid and alkaline media that zinc is considered an amphoteric element, as it is aluminium.

The most used route to extract Zinc from ores is the electrolytic process consisted of ore concentration through froth flotation, transformation of zinc sulphide in oxide through fattening, transformation of oxide in sulphate by acid leaching and then electrowinning. Another route for sulphate achievement is through bioleaching. It is a useful alternative due its capacity of reducing initial steps since it is not a batch process. Once the metal is obtained, it can be industrially applied.

The zinc coating is considered the main industrial application of this metal, representing approximately half of the destination of its production[6]. Depending on the application, the thickness of this coating may vary from 0.13 to 4.0mm. It is also used in galvanizing and relies on a metal coating on other materials such as iron/mild steel to protect them from oxygen, water and salts that corrode these materials affecting their applicability.

## OBJECTIVE

This technical contribution aims at extracting zinc out of galvanized mild steel scraps by two acid and alkaline media taking into consideration the amphoteric characteristic of zinc as well as achieving a final product with industrial value through electrowinning.

## 2. METHODOLOGY

As zinc is an amphoteric element, two recovery routes are possible: the acid and alkaline routes. The material used in this study consisted of pieces of galvanized steel sheets cut to the dimensions of 2 x 2 cm, which were used in a rotating drum immersed in the different leaching solutions (i.e., sulphuric acid and sodium hydroxide medium). The zinc content in the abovementioned scrap was 1.5%, which was calculated from the acid digestion of a representative sample of such scrap and the liquor analysed by atomic absorption spectrometry.

### 2.1 Alkaline route

The alkaline route is based on the dissolution of zinc in sodium hydroxide solution by separating zinc-free galvanized steel and generating a solution of sodium zincate (Na2ZnO2). This solution is then acidified with sulphuric acid to pH 1.5 to form an acid solution of zinc sulphate from which the zinc is electrowon in its metallic form. In this option only zinc is dissolved, as sodium hydroxide does not attack the mild steel. However, it may not be as effective as the sacrificial metal oxidizes to protect the substrate forming an adherent and poorly porous oxide layer (ZnO), which does not react with the alkaline medium, reducing the extraction capacity of that reagent.

### 2.2 Acid route

Compared to the previous route, the acidic route dissolves zinc using sulphuric acid solution producing liquor bearing ferrous sulphate ($FeSO_4$) and zinc sulphate ($ZnSO_4$). Ferrous sulphate can be oxidized to ferric sulphate using hydrogen peroxide ($H_2O_2$). This solution of ferric and zinc sulphate is then treated with sodium hydroxide to pH 3.0, with vigorous stirring, where the iron is precipitated as goethite (FeOOH), and the zinc is subsequently recovered by electrolysis. In spite of the contamination with iron, this route is more effective since the acid attacks all the zinc coating (*i.e.*, Zn and ZnO), also allowing the iron recovery. The latter, in the form of goethite (*i.e.*, FeOOH), high added value pigment; maghemite ($Fe_2O_3$, $\gamma$-$Fe_2O_3$) with magnetic properties.

For this first step of the zinc recovery, operational parameters were tested in order to combine them and thus to find the best condition to proceed with obtaining the metal. A Full Factorial Planning $2^3$ was carried out with the objective of evaluating what should be the most appropriate combination of factors for the zinc extraction from galvanized steel scrap. The factors tested were sulphuric acid concentration (0.1 and 0.3 M), reaction time (30 and 60 minutes) and rotation speed of the hexagonal drum (30 and 60 rpm). The reaction system used can be seen in Figure 1, consisting of a rotating drum, with a magnetic pump, for homogenizing the solution. In addition, it is important to note that all tests were performed according to a factorial planning and subsequent statistical treatment of the results.

**Figure 1: Reaction system for the leaching tests.**

## 3. RESULTS AND DISCUSSION

Samples of approximately 230g of scrap were reacted with sulphuric acid or sodium hydroxide, according to the process used. Aliquots were removed every 10 minutes in order to monitor the zinc extraction analysing them by atomic absorption spectrometry.

By knowing data such as sample mass, zinc content in the galvanized steel studied, aliquot volumes and analytical results, it was possible to calculate the percentage of extraction of the metal according to the variation of the parameters already mentioned. Table 1 shows the combinations of factors chosen for being evaluated in the present study, as well as the respective zinc extraction for each combination. As expected, the acidic route makes it possible to extract zinc from both the zinc metal and the zinc oxide layer, transforming both phases into zinc sulphate.

**Table 1. Zinc extraction during the acid and alkaline leaching processes.**

| Test | Replicate | Reagent Concentration (M) | Rotation speed (rpm) | Time (min.) | (%) Zn extraction Acid Route | (%) Zn extraction Alkaline route |
|---|---|---|---|---|---|---|
| 1 | 1 | 0.1 | 30 | 30 | 64.06 | 1.77 |
| 2 | 1 | 0.3 | 30 | 30 | 79.34 | 5.74 |
| 3 | 1 | 0.1 | 60 | 30 | 78.41 | 1.84 |
| 4 | 1 | 0.3 | 60 | 30 | 80.94 | 7.03 |
| 5 | 1 | 0.1 | 30 | 60 | 80.41 | 2.56 |
| 6 | 1 | 0.3 | 30 | 60 | 85.19 | 15.70 |
| 7 | 1 | 0.1 | 60 | 60 | 85.82 | 3.77 |
| 8 | 1 | 0.3 | 60 | 60 | 83.86 | 12.09 |
| 9 | 2 | 0.1 | 30 | 30 | 57.91 | 1.73 |
| 10 | 2 | 0.3 | 30 | 30 | 77.57 | 7.37 |
| 11 | 2 | 0.1 | 60 | 30 | 78.45 | 2.43 |
| 12 | 2 | 0.3 | 60 | 30 | 80.36 | 8.65 |
| 13 | 2 | 0.1 | 30 | 60 | 94.14 | 2.94 |
| 14 | 2 | 0.3 | 30 | 60 | 92.47 | 11.94 |
| 15 | 2 | 0.1 | 60 | 60 | 89.83 | 3.40 |
| 16 | 2 | 0.3 | 60 | 60 | 85.94 | 13.61 |

From the analysis through the *Statistica* software 12 it was observed that the factors reagent concentration and rotation speed, the concentration-rotation interaction (represented by 1 by 2) and the interaction between the three factors (concentration, rotation and time, represented by 1 * 2 * 3 in Figure 2) are not statistically significant within the levels studied. This does not mean, however, that these factors and interactions do not interfere with zinc extraction. It is also possible to verify through the Pareto Chart (Figure 2), which factors and interactions present statistical relevance, comparing graphically the data contained in the ANOVA Table (data not shown). Factors and interactions whose bars are to the right of $p = 0.05$ are statistically significant. As can be observed in the Pareto chart the most relevant parameter was the reaction time.

In addition to the zinc concentrations in each aliquot, the concentrations of iron in solution during the acid route were analysed. It is noticed that the concentration of ferrous sulphate increases as the reaction goes on, and that from the moment that the majority of the zinc coating is transformed into sulphate, the iron content increases relatively because it is directly attacked by the sulphuric acid, increasing its reactivity.

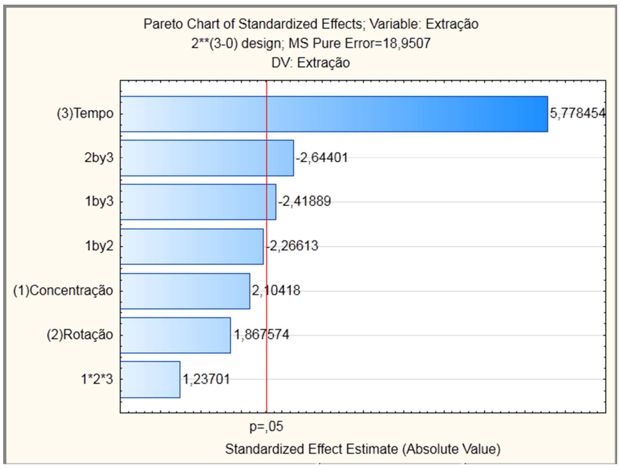


**Figure 2:** Pareto Graph for the factorial design $2^3$.

In relation to the tests with alkaline solution, the results of zinc extraction were not so expressive since the layer of zinc oxide formed in the surface of the metallic zinc, as protection mechanism of the mild steel substrate, is not soluble in alkaline medium, thereby retarding the dissolution of the metallic zinc.

With the acid and alkaline leachates obtained in the leaching tests, zinc electrowinning preliminary tests were accomplished using aluminum cathode and DSA® anode (Dimensionally stable anodes), with very promising results. It was observed, running the electrowinning tests, using the acid liquors as the electrolyte of the cell that the current efficiency for the zinc electro-deposition to occur decreases over the electrolysis time due to the depletion of zinc concentration as the electrolysis goes on, which stimulates the hydrogen evolution out of the $H^+$ ions reduction. As a consequence of such cathodic reactions the specific energy consumption for the zinc reduction increases, as shown in Figure 3.

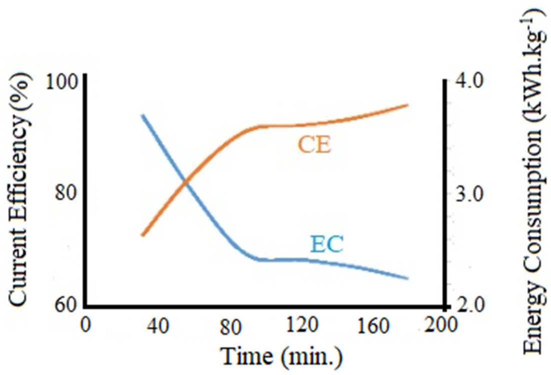


**Figure 3:** Variation of current efficiency and energy consumption over zinc electrowinning.

## 4. CONCLUSION

The acidic route is quite attractive in terms of the extraction of zinc from both the zinc and the zinc oxide of said scrap with the possibility of addition of iron dissolved in different pigments (*i.e.*, goethite and maghemite). However, the alkaline route has proved to be ineffective due to the fact that part of the metallic zinc layer is transformed into zinc oxide as a result of the carbon steel substrate protection mechanism, which prevents all contained zinc from being solubilised in the formation of soluble zinc species (*i.e.*, zincate – $ZnO_2^{2-}$). Regarding the precipitation of iron as goethite, this occurred very satisfactorily by raising the pH of the acidic liquorsurroundings 3 by adding sodium hydroxide and vigorous stirring. According to the preliminary electrowinning tests, using the acid liquors in particular, the current efficiency for the zinc electro-deposition decreases as the electrolysis goes on, causing the energy consumption to increase consequently. This means that it is not that cost effective to electrowin the whole available zinc in solution bearing in mind that the acidity increases over electrolysis time, and such electrolyte can be further used for leaching another batch of galvanized steel scrap.

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