

Recovery of Zinc from Galvanized Scraps

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Abstract

The stripping of Zn in sulfuric acidic solutions from galvanized steel products obtained from industry and the removal of impurities from this solution and the conditions required for Zn recovery were experimentally investigated. According to the results, it is possible to completely strip Zn from used galvanized steel products by using sulfuric acid with a pH value of up to 0.2. A solution that contains Zn over 80-85 g/l and Fe 0.2 g/l can be produced by repeated stripping and it is possible to obtain ZnSO₄ from the solution by adding volatile liquid (ethyl alcohol). The precipitated Zn compound is ZnSO₄.H₂O. This compound contains 36.4% Zn and 0.002% Fe and is a raw material pure enough for commercial use. The ethyl alcohol used to obtain ZnSO₄.H₂O from the rich stripping solution is recovered with 90% efficiency through distillation at 78°C for 20 min. This process optimized by the experiments allows for the manufacture of saleable products and causes no environmental problems.

Key words: Galvanize, Scrap, Stripping, Zinc Salt

Introduction

Galvanizing is a coating process applied in order to prevent iron-based materials from corroding. Galvanizing is applied by electrolytic coating or hot-dipping into a zinc bath. Hot-dip galvanizing is one of the most common and economical coating methods and it is particularly used to coat steel. The reaction between the substrate and the coating material forms an alloy layer that provides a sound physical and mechanical connection between the coating material and the substrate.

According to the galvanic series, iron is cathodically protected while zinc dissolves, as it is more active and this way iron- and steel-based material can be used without any damage until all the zinc is consumed.

After the zinc layer on the galvanized piece is consumed, the piece is scrapped or it is regalvanized if possible. Before this treatment, degalvanization is a must. When the galvanized material dissolves in H₂SO₄ during degalvanization, the following re-

actions take place:



Discarding the solution of degalvanizing after a simple neutralization process causes environmental pollution and the metals of this solution cannot be recovered. In order to recover the Zn from a solution that has undergone degalvanization, it is necessary to remove the Fe in the solution. After Fe is removed from the solution, it is possible to recover Zn from the solution as a metal or compound.

In this work, the stripping of Zn from used galvanized steel products in H₂SO₄ solutions, cleaning the stripping solution of impurities and recovering Zn from purified solution were experimentally investigated. The recovery of Zn from the solutions as a saleable pure compound was the basic aim of this experimental work.

Experimental Work

Raw Materials

In these experiments, galvanized sheets and scraps obtained from industry were used. The zinc contents of the galvanized sheets and scraps are shown in Table 1.

The galvanized scraps used in these experiments were steel pieces brought to galvanizing units for galvanizing. The steel sheets were commercially available samples of galvanized sheets with a thickness of 1 mm.

Materials and Equipment

In the experiments carried out in order to recover zinc from used steel pieces, analytically and technically pure enough H_2SO_4 and various chemicals were used. For electrochemical analysis electrodes made of refined copper, volatile organic liquid (ethyl alcohol) and distilled water were used.

Contact thermometer controlled Framo-Gerätetechnik heater + magnetic stirrer were used and Ika Werk RW20 stirrer for heating and stirring the solutions; Leontech LT-830D avometer for electrochemical measurements; Elektro-Mag M3 distillation unit for pure water production; Schott-CG840 pH meter for pH measurements; Perkin-Elmer 1100B atomic absorption spectrophotometer for chemical analysis of solutions; Philips X-ray diffractometer for characterization of end products; Sartorius scale for weighing and Carbolite oven for drying the end products.

The other equipment used in this work were a glass distillation unit for ethyl alcohol, a filtration set that consisted of a vacuumed nuche Erlenmeyer, rozantel and water tromp and some other standard laboratory glassware.

Experimental

Figure 1 shows the flow sheet for the experiments carried out for the recovery of zinc from galvanized

scraps.

Galvanized pieces were stripped in an acidic solution in a beaker. The complete dissolution of Zn and minimum dissolution of Fe during the stripping process were check by electrochemical measurement between the stripping plate and the Cu cathode plate. Fe going into the solution was precipitated as goethite. In this process, ZnO as a neutralizer and H_2O_2 as an oxidant were used. Zn was precipitated from the purified solution by the addition of ethyl alcohol. After the solid/liquid separation, ethyl alcohol was recovered by distillation. The barren solution was returned to the first step of the process.

The Zn content of the galvanized pieces was determined according to TS 914. After appropriate dilution, the concentration of metal in the solution was determined in an atomic absorption spectrophotometer. Solid analysis was also performed in an atomic absorption spectrophotometer after dissolving in an acidic solution. Figure 2 shows the potential controlled set-up for zinc stripping. Fe was precipitated as goethite and was removed from solution by filtration. Then, the pure zinc was precipitated by the addition of ethyl alcohol into the purified solution. After solid/liquid separation, the solution free from zinc was distilled for the recovery of ethyl alcohol and the remaining solution was fed back into the system.

Results

Experiments of Zn stripping in H_2SO_4

Figures 3-9 show the change in the quantity of Fe and Zn, as a function of time, that was transferred to the solutions of different pH levels after Zn stripping from used galvanized sheets in H_2SO_4 solutions with pH values ranging from 0 to 0.6 and the potential shift obtained through the electrochemical measurement performed using a copper electrode. The experimental data for these figures are summarized in Table 2. Among the experimental analysis shown in Table 2, the change as a function of time is given in graphical form only for the experiments performed at pH levels up to 0.6 due to the fact that after pH 0.6 stripping times were very long.

Table 1. Zn contents of the steel samples used in stripping experiments

Sample	Description	Zinc Quantity (g/m ²)
Sheet-1	Galvanized Scrap Sheet	17.3
Sheet-2	Galvanized Scrap Sheet	10.3
Steel piece	Galvanized Scrap Piece	550

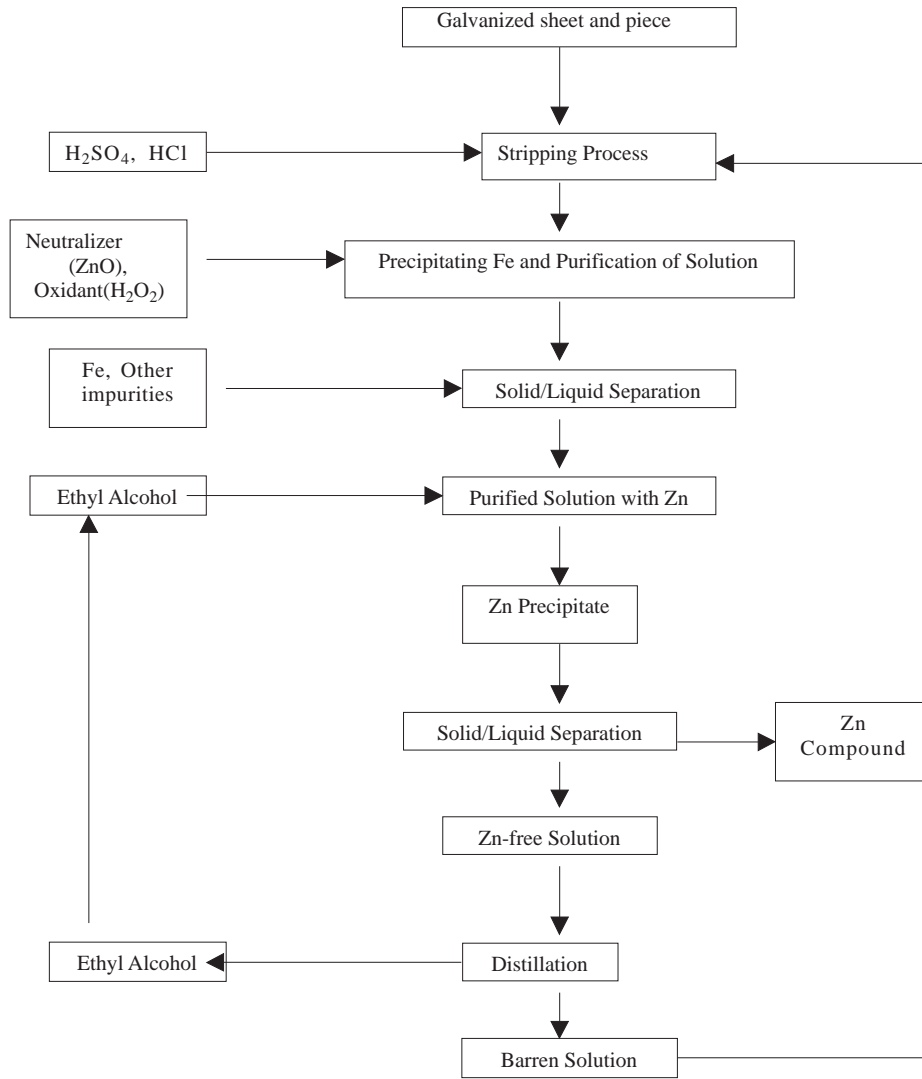


Figure 1. The flow sheet for the experiments carried out for the recovery of zinc from galvanized scraps.



Figure 2. The potential controlled set-up for zinc stripping.

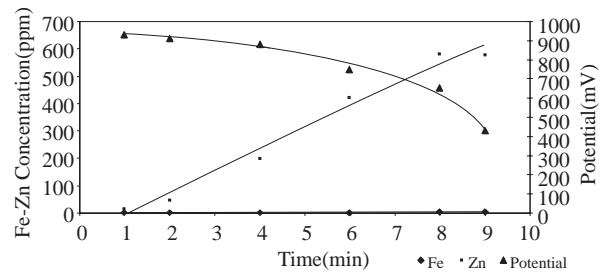


Figure 3. The change in Fe and Zn quantity as a function of time and potential, in a Zn stripping process performed using a Cu cathode in H₂SO₄ with a pH level of 0.

Table 2. The change in potential, time and quantity of Fe and Zn going into the solution and Zn stripping efficiency, as a function of pH level, in a Zn stripping process performed using a Cu cathode in H₂SO₄.

pH	Zn Quantity in Piece (mg)	Potential (mV)	Time (min)	Fe Content (ppm)	Zn Content (ppm)	Zn Stripping Efficiency (%)
0	602	430	6	1	600	99.66
0.1	635	421	8	1	631	99.37
0.2	617	440	10	2	613	99.35
0.3	635	448	14	4	629	99.05
0.4	625	456	16	3	620	99.21
0.5	629	445	18	3	622	98.88
0.6	591	432	20	3	584	98.76
0.7	566	420	45	3	559	98.73
0.8	649	436	53	4	639	98.45
0.9	606	590	70	4	588	97.03
1	473	705	72	4	319	67.44

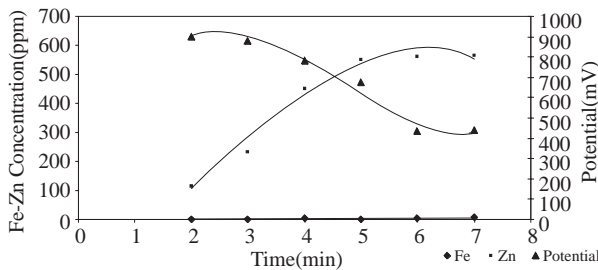


Figure 4. The change in Fe and Zn quantity as a function of time and potential, in a Zn stripping process performed using a Cu cathode in H₂SO₄ with a pH level of 0.1.

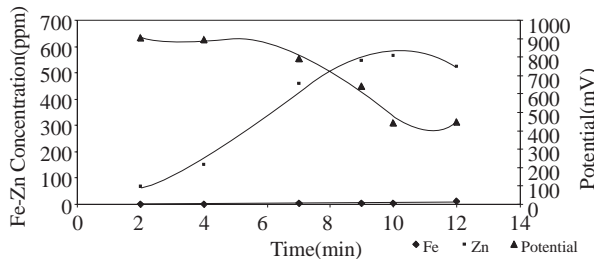


Figure 5. The change in Fe and Zn quantity as a function of time and potential, in a Zn stripping process performed using a Cu cathode in H₂SO₄ with a pH level of 0.2.

When the diagrams showing the data obtained through the stripping experiments in H₂SO₄ and Table 2 are examined, it is seen that the stripping is optimal up to pH 0.2. After this point, the stripping time and the amount of Fe going into the solution increase. The electrochemical analysis shows that

in all pH levels the stripping of Zn is completed in a potential range between 420 and 440 mV. If the stripping is continued after reaching this potential range, the amount of Fe going into the solution increases. Therefore, stripping in H₂SO₄ solutions is a function of acid concentration. At high H₂SO₄ concentrations, e.g. pH 0-0.2 dissolution of 1-2 ppm (mg/l), Fe is accompanied by the stripping of all Zn in the solution within 6-10 minutes.

The final potential value at the point where dissolution of Zn is completed and Fe goes into the solution is in the range of 420-440 mV, which corresponds to a potential reaction of half cell reaction of $Fe^{2+} + 2e^- = Fe^0$. (Bor, 1989; Pawlek, 1983). Thus, during the stripping experiments, the movement at which the dissolution of Zn is completed and Fe starts going into the solution can be correctly established through electrochemical measurements. Should the pH level in starting solution be kept over 0.2, the stripping of Zn takes a lot longer. This longer stripping time also promotes the transfer of more Fe into the solution.

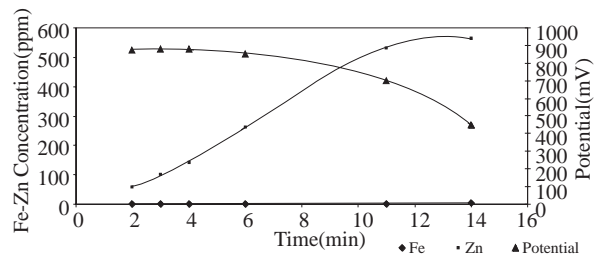


Figure 6. The change in Fe and Zn quantity as a function of time and potential, in a Zn stripping process performed using a Cu cathode in H₂SO₄ with a pH level of 0.3.

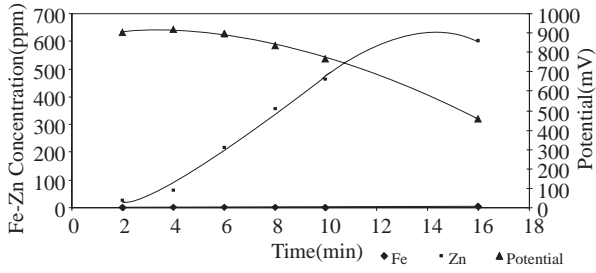


Figure 7. The change in Fe and Zn quantity as a function of time and potential, in a Zn stripping process performed using a Cu cathode in H₂SO₄ with a pH level of 0.4.

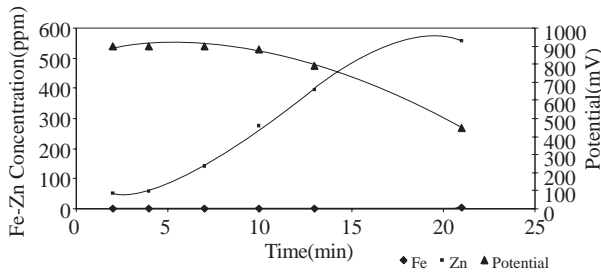


Figure 8. The change in Fe and Zn quantity as a function of time and potential, in a Zn stripping process performed using a Cu cathode in H₂SO₄ with a pH level of 0.5.

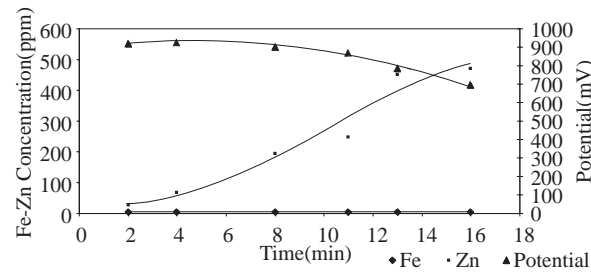


Figure 9. The change in Fe and Zn quantity as a function of time and potential, in a Zn stripping process performed using a Cu cathode in H₂SO₄ with a pH level of 0.6.

Kinetics of Zinc Stripping

After establishing the optimal pH conditions, some experiments were performed to examine the kinetics of Zn stripping. In these experiments, at pH 0, the temperature was increased from 40°C to 70°C with 10°C increments, and the stripping, accompanied by electrochemical measurements using a copper electrode, was continued until the potential dropped to

the range 420-440 mV. For kinetics calculations, the following first order dissolution rate equation was used:

$$k = \ln(1 - \alpha)$$

where k is the stripping rate constant (1/time), and α the stripping efficiency. The k value calculated by plotting the change in α as a function of temperature for various temperatures was then placed in the Arrhenius equation $k = A e^{(-E_A/RT)}$ and activation energy was calculated at $\ln k - 1000/T$ change where A is constant, E_A is activation energy (kJ/mol), R is gas constant (8.31 kJ/mol K) and T is temperature (K) (Şeşen, 1998)

For this group of experiments, the change in stripping efficiency (α) as a function of time and temperature is shown in Table 3. The time- $\ln(1 - \alpha)$ change plotted using this table is shown in Figure 10.

Table 3 shows the change in stripping efficiency as a function of time and temperature.

Table 3. Time-α change for each temperature (α = stripping efficiency)

Time(min)	40°C α value	50°C α value	60°C α value	70°C α value
0.5	0.03	0.08	0.11	0.29
1	0.14	0.26	0.29	0.62
1.5		0.41	0.56	0.83
1.75				0.85
2	0.41	0.59	0.69	0.86
2.5		0.71	0.79	0.91
3	0.63		0.82	
4	0.83			
5		0.88		
6	0.89			

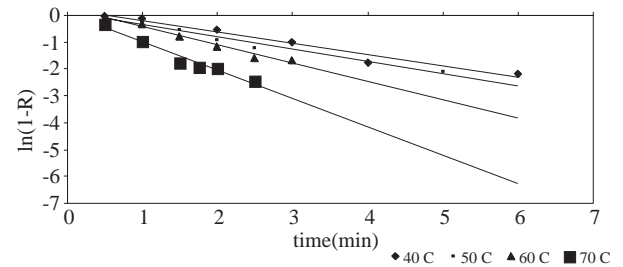


Figure 10. $\ln(1 - \alpha)$ change as a function of time

The stripping rate constants calculated from this figure are shown in Table 4. The $\ln(k)-1000/T$ change obtained by placing the calculated relative stripping constants in Arrhenius equations are shown in Figure 11.

Table 4. Temperature-slope (k) relationship

Temperature(T)°C	Slope(k)(1/min)	lnk
40	0.42	-0.86
50	0.46	-0.78
60	0.68	-0.38
70	1.06	0.06

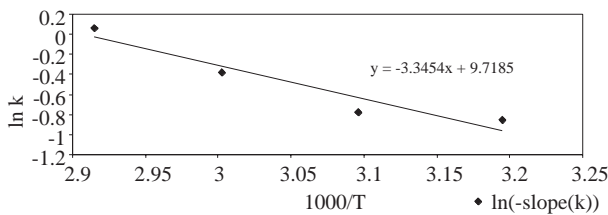


Figure 11. $\ln(k)-1000/T$ change

The slope of this linear line is equal to $-E_A/R$ and the activation energy calculated from this is 27.21 kJ/mol. This quite low activation energy level indicates that Zn stripping is a diffusion-controlled process and shows that the Zn stripping processes performed at pH levels up to 0.2 will rapidly occur. Therefore, the short stripping times found by the stripping experiments are also confirmed by kinetic energy level (Latimer, 1953).

Experiment of Goethite Precipitation

After the experimental optimization of Zn stripping processes, in order to recover the Zn from stripping solutions, repeated Zn stripping experiments were performed using the same solution. As a result of these repeated stripping experiments, while Zn in the solution was increased up to 80-85 g/l, Fe went into solution at 0.2 g/l. Since the presence of Fe in the solution would decrease the purity of the Zn compound, the removal of Fe from the solution was executed by the goethite precipitation method (Davey, Scott, 1976). The reason for choosing this method was that while Fe was precipitated as goethite, Zn could stay in the solution without precipitating.

In goethite precipitating experiments the Fe in the solution, present as Fe^{2+} , was first oxidized by the addition of H_2O_2 (Sönmez, 1999) and after oxidation the pH of the solution stayed in the range

0.4-0.6. Then, by technical zinc oxide addition, the solution was neutralized up to the pH level range 2-3, which is the precipitation pH level of goethite. The ZnO quantity used was 1.5-2% of solution in weight. After neutralization, the change in Fe quantity in the solution as a function of time and pH are shown in Figure 12. As can be seen from the figure, in approximately 15 minutes almost all the Fe precipitated as goethite and the solution was purified down to a level of 0.5 mg/l Fe.

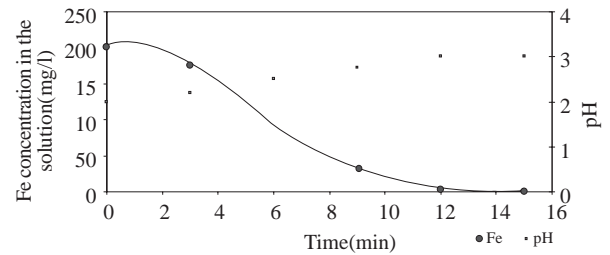


Figure 12. The change in the Fe quantity in the solution as a function of time. (The starting Fe concentration 200 ppm, stirring rate 400 r.p.m.)

Experiments for Recovery of Zn from Solution

The production of zinc sulfate by breaking the ligand structure by the addition of ethyl alcohol, in order to recover Zn from zinc sulfate solution obtained after repeated stripping and removal of Fe, was executed in this group of experiments (Zaromb and Lawson, 1994). The results obtained through the experiments performed are as follows:

In the first group of experiments, the effect of solution pH on zinc recovery efficiency was investigated. The change in zinc precipitation efficiency as a function of pH obtained by reacting 1 unit volume solution with 2.5 unit volume solution is shown in Figure 13.

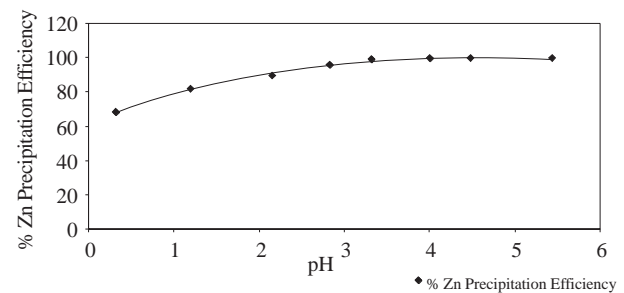


Figure 13. The effect of pH on zinc recovery efficiency (stirring rate: 500 r.p.m., 2.5 unit ethyl alcohol per unit volume solution, 100 g/l Zn).

As can be seen from the related diagram, zinc precipitation efficiency increases up to 99% when pH increases up to 3 and this efficiency is not affected by any further pH increases. The precipitation of Zn is easier when the pH of the solution is around 3 because the ligand structure of water starts to weaken at this pH level.

The effect of quantity of ethyl alcohol added into the solution on zinc recovery efficiency was investigated in the second group of experiments after the optimum pH was established. For the experiments performed at pH 3, the change in zinc efficiency with increases in the liquid/solution volume ratio from 1 to 2.66 is shown in Figure 14. As can be seen from the diagram, in order to obtain 99% zinc precipitation efficiency, the ethyl alcohol/solution volume ratio should be 2.5. This ethyl alcohol quantity allows the precipitation of all Zn in a solution that contains 100 g/l Zn. In other words high enough breaking of the ligand structure is done by means of ethyl alcohol.

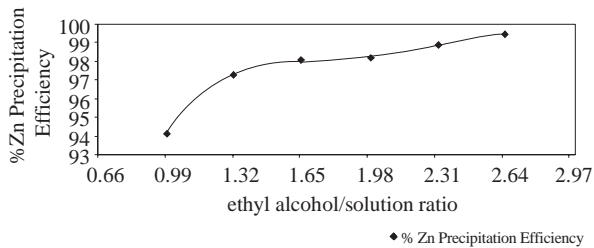


Figure 14. The effect of the ethyl alcohol/solution volume ratio on zinc recovery efficiency (pH = 3, stirring rate 800 r.p.m., solution contains 100 g/l Zn; time:15 min).

The last group of the experiment was performed to investigate the effect of initial zinc concentration on zinc precipitation efficiency by the addition of ethyl alcohol at a constant pH and constant ethyl alcohol/solution volume ratio. As can be seen in

Figure 15, it is established once again that when the pH of the solution is kept at 3 and the ethyl alcohol/solution volume ratio is 2.5/1, this ethyl alcohol quantity is sufficient for 100 g/l Zn concentration.

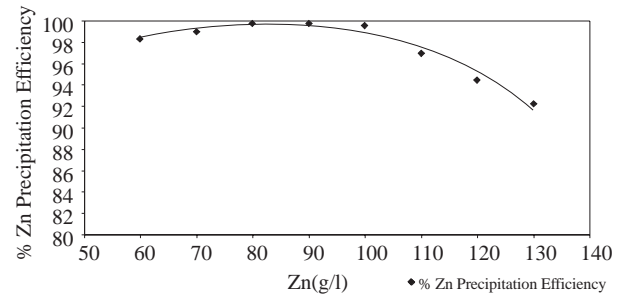


Figure 15. The change in zinc precipitation efficiency as a function of zinc concentration in the solution (ethyl alcohol/solution volume ratio: 2.5/1, pH = 3, stirring rate 800 r.p.m., time 15 min).

Distillation of Ethyl Alcohol and Product Characterization

Distillation of the remaining ethyl alcohol in a barren stripping solution was optimized through some experiments. Table 5 shows ethyl alcohol efficiency as a function of distillation temperature.

As can be seen from the table, in distillation processes performed at 76-80°C for 20 minutes, the range 78-79°C is the most optimal temperature. At this temperature ethyl alcohol of 95-97% purity can be recovered with 90% efficiency. At higher distillation temperatures, in spite of the increase in distillation efficiency, the purity of ethyl alcohol falls down to 80-85%.

The X-ray diffractogram of the product precipitated from stripping solution by the help of ethyl alcohol (Figure 16) shows that this compound is $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$.

Table 5. Distillation efficiency obtained at different temperatures

Temperature (°C)	Time (min)	Distillation Efficiency
76	20	81
77	20	87
78	20	91
79	20	90
80	20	92 (dilluted with water)

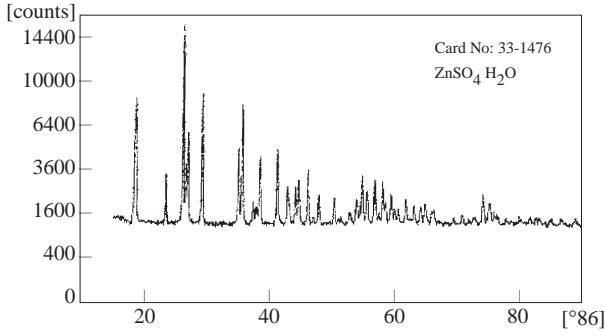


Figure 16. X-ray diffractogram showing that the precipitated Zn compound is pure $ZnSO_4$ containing 1 mol crystal water.

This zinc sulfate compound with 1 mol crystal water is a quite pure compound containing 36.4% Zn and 0.002% Fe.

Conclusion

Up to pH 0.2, the stripping of all Zn from used galvanized steel products in H_2SO_4 is possible. In repeated stripping solutions, it is possible to obtain solutions over 85 g/l Zn and up to 0.2 g/l Fe. Firstly, by oxidation with H_2O_2 , and then by neutralization with commercial ZnO, Fe in $ZnSO_4$ solutions concentrated by repeated stripping can be precipitated

as goethite to concentration levels of down to about 0.5 mg/l.

The Zn in Fe-free purified stripping solution, containing 100 g/l Zn as a result of neutralization, can be precipitated as zinc sulfate by the addition of ethyl alcohol that brings the ethyl alcohol/solution volume ratio to 2.5/1. In the precipitation process performed by means of ethyl alcohol, over 99% precipitation efficiency can be attained in 15 minutes by stirring the solution at room temperature at pH 3.

By distilling a barren solution for 20 minutes at $78^\circ C$, obtained after the production of $ZnSO_4 \cdot H_2O$ from rich stripping solution, ethyl alcohol with 95-97% purity can be recovered with 90% efficiency. Ethyl alcohol produced by distillation can be used again for $ZnSO_4 \cdot H_2O$ production. The pH of the waste solution coming from distillation is around 3-3.5 and can contain 1-2 g/l Zn. This solution can be recycled to a stripping stage after acidification.

The process explained above, along with the main optimization conditions, is one that will yield a saleable product and not cause environmental problems. This process, which targets the stripping of Zn from used galvanized pieces and the recovery of this Zn as a pure compound, can be easily applied with a small investment.

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