



Recovery of zinc from industrial waste pickling liquor



Abhishek Pathak*, Anurag Roy, Manindra Manna

Research & Development, Tata Steel, Jamshedpur 831007, Jharkhand, India

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ABSTRACT

The constantly increasing global demand of zinc metal along with the decreasing zinc ore reserves has led to an upward trend of zinc production from secondary sources. Galvanizing industry generates byproducts and wastes containing zinc in the form of intermetallic compounds or oxides (zinc dust). One such byproduct, waste pickling liquor (WPL) is generated in galvanizing industry during the pickling of defective galvanized material. WPL contains Zn and Fe in ionic form and is discarded after neutralization. In the present work, chemical precipitation method is used to recover zinc from WPL; with an objective to retain maximum possible iron within the WPL solution. The effect of precipitating agent concentration, number of reactions steps, temperature and stirring speed were considered to determine process parameters for maximum zinc recovery. The iron rich WPL solution with negligible quantities of zinc is a valuable ingredient for production of red oxide pigment. Thereby, two products are obtained by adopting this technique: (i) Zinc rich precipitates and (ii) iron rich pickling liquor. X-ray diffraction (XRD) analysis of precipitates (heated at elevated temperature), shows that zinc oxide and zinc ferrite phases were formed from the zinc rich precipitates.

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1. Introduction

In the last decade there is an upward trend for the global demand of zinc due to increase in number of galvanizing lines and battery production lines worldwide (Kunicky et al., 2008). The ore reserves for zinc are depleting gradually contributing to steep increase in cost of zinc. To overcome the above mentioned problems, zinc production from secondary sources is increasingly being explored and researched worldwide. One such secondary source of zinc is the waste pickling liquor (WPL) generated during the degalvanizing process (Sönmez et al., 2003). Defective galvanized product is pickled in dilute sulphuric acid bath to dissolve the zinc coating and the resulting material is sent for re-galvanizing. The process of dissolving the zinc coating in pickling solution is called degalvanizing.

The general practice in industry is to discard the pickling solution of degalvanizing after neutralizing treatment. This results in environmental pollution and loss of Fe and Zn metal ions. The recovery of the metal ions from waste can provide economic benefits and reduce pollution (Serdar and Ercan, 2002).

Pyrometallurgy and hydrometallurgy are the two most extensively used processes for recovery of metal from secondary sources. Pyrometallurgy is an energy intensive process and requires higher installation and maintenance costs. Similarly, in the earlier years; hydrometallurgical processes also used to be expensive as it involved long procedures, lower efficiency of metal recovery, heavy consumption of chemicals

and secondary pollution due to wastewater discharge. But in recent years, researchers have succeeded in reducing the number of process steps, increasing metal recovery efficiency and possible recovery of leachants to make hydrometallurgical processes more feasible for industrial scale metal recovery (Sayilgan et al., 2009; Peng et al., 2008). The solvent extraction and chemical precipitation techniques are now well established and efficient methods for recovering metals.

The solvent extraction method has been explored by researchers for extracting zinc over iron from spent pickling solution. Ortiz et al. (2010) reported a maximum zinc over iron recovery efficiency of 146 (g Zn/g Fe) from spent hydrochloric acid solution using Tributyl Phosphate (TBP) as extracting agent and water as back recovery agent (BEX), following a membrane based solved recovery process. Mansur et al. (2007) found that Tributyl phosphate (TBP) and Cyanex 301 [bis (2,4,4-trimethylpentyl) dithiophosphinic acid] could selectively remove zinc with nearly 90% efficiency while iron with approximately 10% efficiency from spent hydrochloric acid pickling solution. Martin et al. (2001) studied the selective zinc recovery from a multi-cationic leached liquor (pH 2), with di-(2-ethylhexyl) phosphoric acid (D2EHPA) as extractant while Vahidi et al. (2009) found that almost all zinc could be extracted at pH of 2.5 in an aqueous solution of 20% w/w D2EHPA in kerosene. Regel-Rosocka and Wisniewski (2011) reported selective recovery of zinc over iron in a three stage process using Trihexyl (tetradecyl) phosphonium chloride (Cyphos IL-101) – a phosphonium ionic liquid. Zinc oxalate precipitation was reported as nearly 100% after three stage process while iron recovery efficiency was 40%. Solvent extraction processes for zinc recovery have the advantages of easy operational conditions, low energy consumption and good

* Corresponding author.

E-mail address: abhishek.pathak@tatasteel.com (A. Pathak).

separation effect but at the same time solvent extractants and ionic liquids are very expensive and consequently might result in too high treatment costs when scaled up in industry practice (Xu et al., 2008).

Compared to solvent extraction, chemical precipitation process is a simpler and cheaper method to separate metals from leach liquor. Kunicky et al., 2008 studied the effect of treatment time in the separation of zinc from zinc rich galvanic sludge in the form of basic zinc carbonate at pH of 8.5. Dvorak and Jandova (2005) further optimized the zinc carbonate precipitation at 40 °C by studying the effect of temperature on precipitation and used electrowinning process for subsequent recovery of zinc metal. For both, solvent extraction and chemical precipitation methods, most of the work is reported for spent hydrochloric acid pickling solution while the present work deals with selective zinc recovery over iron from spent sulphuric acid pickling solution, which is not much reported.

The main objective of present work is to determine a simple and easy extraction process which can be up-scaled to industry level. In the present work, chemical precipitation method is adopted to recover zinc from waste pickling liquor (WPL) using oxalic acid as precipitating agent; with aim to retain iron within the WPL solution. Oxalic acid was selected as precipitating agent based on the solubility product constant (K_{sp}) values for iron oxalate and zinc oxalate, which are 2×10^{-7} and 1.4×10^{-9} , respectively. It was expected that iron oxalate formed during the recovery treatment will remain in the solution in dissolved form. The effects of oxalic acid concentration, number of reaction steps, temperature variation and stirring speed were studied to optimize zinc recovery conditions. The zinc rich precipitates were characterized by XRD to detect the phases formed and their proportions.

The iron rich waste pickling liquor can be supplied to red oxide pigment manufacturing industry. The prerequisite conditions necessary to produce red oxide pigment from WPL are as follows: (i) Iron in the range of 100–150 (g/L) (ii) zinc <1.5 (g/L) and (iii) pH <2. The typical manufacturing process of red oxide pigment includes the treatment of high iron containing WPL solution with sodium hydroxide under controlled pressure and temperature conditions to precipitate iron hydroxide.

2. Materials and methods

2.1. Analysis of initial WPL

Chemical analysis of WPL solution, before and after precipitation experiments, was done volumetrically by standard methods as mentioned by Vogel (1989). The results are shown in Table 1. In Table 1, Fe (T) stands for total iron present in the WPL solution while Fe (II) represents the amount of Fe²⁺ ions in the solution. The difference of Fe (T) and Fe (II) was taken as Fe (III). The concentrations of zinc and iron were also determined by Atomic Absorption Spectroscopy (AAS) technique (make – Thermo, AAC/– 6) to re-check the chemical analysis results. The WPL is used for pickling of steel and galvanized tubes in a mechanized industrial plant. There is a negligible possibility of presence of impurities in the WPL. In AAS analysis, along with Zn and Fe, minute level impurity of Ni (9.5 mg/L) and Mn (128.9 mg/L) was found.

2.2. Precipitation experiment

Precipitation experiments were performed in two stages. In the first stage, effect of varying the temperature (25 °C and 50 °C) and stirring speed (0; 100 and 500 rpm) on Zn and Fe recovery efficiency was

Table 1
Chemical analysis of WPL.

Sample	Fe (T) (g/L)	Fe II (g/L)	Fe (III) (g/L)	Fe(II)/ Fe(III)	Zn (g/L)	pH
Initial WPL	11.2	10.5	0.7	15	94.77	1

studied for a constant Zn ion: Oxalic acid (molar ratio) of 1:1. In the second stage, effect of oxalic acid concentration and number of reaction steps was examined at the precipitation conditions determined from the first stage experiments.

All the experiments in stage 1 and stage 2 were carried out using 250 mL WPL starting solution in standard lab glass beakers of 500 mL capacity, reaction time of 20 min. In a set of background experiments, the reaction time of 20 min was determined as the optimum time for high zinc extraction efficiency with minimum iron extraction efficiency. The heating and stirring experiments were performed on lab scale 'digital hotplate stirrer' with separate temperature monitor. Solid powder form of oxalic acid (OA) lab grade quality (99% purity, Loba Chemie), was used for all the experiments. Schematic of multiple reaction step treatment process is shown in Fig. 1.

To understand the effect of co-precipitation phenomena on Zn and Fe recovery efficiency, the experiments were performed in one, two and three steps, as shown in Table 2. Experiment numbers 1 to 3 are performed for Zn ion: oxalic acid (molar ratio) of 1:1 and experiment numbers 4 to 6 are performed for molar ratio of 1:1.4. All the experiment numbers 1 to 6 are repeated three times, as shown by the suffix (a), (b) and (c) in Table 2, column 1.

The recovery efficiency of Zn and Fe was calculated as:

Recovery efficiency

$$= \frac{(\text{Initial concentration}) - (\text{Final concentration in residual solution})}{\text{Initial concentration}} \times 100.$$

In 250 mL WPL solution, as per Table 1, the amount of zinc is 23.69 g. In experiment numbers 1 to 3, as per the molar ratio of 1:1, 32.07 g of oxalic acid (in form of solid powder) is added in different steps. In experiment number 1, the total amount of oxalic acid i.e. 32.07 g is added in one single step. In experiment 2, 32.07 g of oxalic acid is added in two steps; in step 1–16.035 g is added and in step 2, 16.035 g is added. Experiment 3 refers to addition of oxalic acid in three steps; in step 1, 40% of oxalic acid is added i.e. 12.83 g, 30% (i.e. 9.62 g) is added in step 2 and remaining 30% (9.62 g) is added in step 3. Summation of quantities of oxalic acid added in steps 1, 2 and 3 gives a total of 32.07 g.

Similarly, experiment numbers 4 to 6 were conducted. In single step process, the total quantity of precipitating agent is added to WPL at one instant, which results in higher chance for co-precipitation. Separation of zinc and iron precipitates become difficult and also the estimation accuracy of reaction in also hampered (Harvey, 2000). In two-steps or multiple-steps process, the phenomenon of co-precipitation is

Table 2
Variation of oxalic acid concentration and number of reaction steps.

Experiment number	Zn:OA ratio (molar ratio)	Oxalic acid addition in multiple steps (g)		
		Step 1	Step 2	Step 3
Expt. 1 (a)	Zn:OA ratio = 1:1	32.07		
Expt. 1 (b)	Zn:OA ratio = 1:1	32.07		
Expt. 1 (c)	Zn:OA ratio = 1:1	32.07		
Expt. 2 (a)	Zn:OA ratio = 1:1	16.035	16.035	
Expt. 2 (b)	Zn:OA ratio = 1:1	16.035	16.035	
Expt. 2 (c)	Zn:OA ratio = 1:1	16.035	16.035	
Expt. 3 (a)	Zn:OA ratio = 1:1	12.83	9.62	9.62
Expt. 3 (b)	Zn:OA ratio = 1:1	12.83	9.62	9.62
Expt. 3 (c)	Zn:OA ratio = 1:1	12.83	9.62	9.62
Expt. 4 (a)	Zn:OA ratio = 1:1.4	44.90		
Expt. 4 (b)	Zn:OA ratio = 1:1.4	44.90		
Expt. 4 (c)	Zn:OA ratio = 1:1.4	44.90		
Expt. 5 (a)	Zn:OA ratio = 1:1.4	22.45	22.45	
Expt. 5 (b)	Zn:OA ratio = 1:1.4	22.45	22.45	
Expt. 5 (c)	Zn:OA ratio = 1:1.4	22.45	22.45	
Expt. 6 (a)	Zn:OA ratio = 1:1.4	16.035	16.035	12.83
Expt. 6 (b)	Zn:OA ratio = 1:1.4	16.035	16.035	12.83

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