Hydrometallurgy 142 (2014) 108–115

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Development of a process for the recovery of zinc sulphate from hot-dip galvanizing spent pickling liquor via two solvent extraction steps

Kwan H. Lum, Geoff W. Stevens, Sandra E. Kentish *

Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010, Australia

ARTICLE INFO

Article history:
Received 17 July 2013
Received in revised form 6 October 2013
Accepted 10 November 2013
Available online 4 December 2013

Keywords:
Solvent extraction
Spent pickling liquor
TBP
D2EHPA
Zinc

ABSTRACT

A process for zinc sulphate recovery from the spent pickling liquor of a hot-dip galvanizing plant is developed. Two solvent extraction steps are used, the first with tributyl phosphate to selectively extract zinc chloride from the spent liquor and the second with di-2-ethylhexyl phosphoric acid (D2EHPA) to transfer zinc from a chloride to sulphate media. The final product of the process is found to meet the specification of low chloride concentration required for electrowinning when the loaded D2EHPA was washed with water. Mathematical simulation was used to further develop the process. Based on a feed concentration of 120 g/L Zn, 60 g/L Fe(II) and 1 mol/L HCl, the simulation predicts that 99.2% zinc can be recovered, yielding a product with 106 g/L Zn.

1. Introduction

In the hot-dip galvanizing industry, pickling baths are used to remove rusts and scales from metal works before they are galvanized. However, the pickling liquor becomes ineffective as the concentration of dissolved metals, mainly iron and zinc, in the bath increases. The highly contaminated spent pickling liquor (5 to over 200 g/L zinc, 60 to 150 g/L iron, and 10 to 80 g/L HCl) (Cook et al., 2011; Kerney, 1994; Stocks et al., 2005) is usually disposed to specialised landfill even though the metals and acid can be recovered. With increasing environmental concerns, legislations and disposal costs, the galvanizing industry is gaining interest in recycling of their spent pickling liquor.

Zinc is the most valuable component of the waste liquor. This zinc can be easily recovered as zinc chloride and used as a fluxing agent within the galvanizing plant. However, only a small quantity of zinc chloride is required for this purpose. Zinc sulphate would have a greater commercial value as it can be readily sold to electrowinning plants for zinc metal production. The development of a process to recover zinc as zinc sulphate is the focus of this paper.

Authors have previously considered the recovery of zinc sulphate using a combination of solvent extraction and evaporation (Reinhardt, 1978; Van Veen, 1981). In this case, zinc chloride is first selectively extracted using tri-n-butyl phosphate (TBP) and then stripped into a sulphuric acid solution. Evaporation is then used to remove the chloride content as HCl vapour. However, this process poses safety concerns and exotic materials are required to resist corrosion by the acid vapours; making the process less economically viable.

Another option is to use a second solvent extraction step to transfer the zinc cations from the chloride to sulphate media, as noted by Kerney (1994) (though the choice of extractant was not reported). This option is similar to the Zincex process which also utilises two solvent extraction steps to produce zinc sulphate for electrowinning purposes from primary or secondary zinc sources (Díaz et al., 2001; Nogueira et al., 1980). The Zincex process uses a secondary amine as the first extractant to selectively extract zinc chloride followed by di-2-ethylhexyl phosphoric acid (D2EHPA) to convert to the sulphate form. However, this process was developed primarily for feed solutions with a low iron content. The presence of a high iron concentration such as in spent pickling liquor has been reported to cause precipitation and poor phase separation with amine extractants (Cierpiszewski et al., 2002).

By substituting the secondary amine with an extractant suitable for processing spent pickling liquor, such as TBP, and keeping the second solvent extraction step with D2EHPA, zinc sulphate can be produced from spent pickling liquor. This option is viable especially since both extractants are commercially available and well understood.

To the best of the authors' knowledge, this process scheme has not been previously examined. As such, there are many processing parameters that require study, such as the composition of the stripping solution for the first solvent extraction step and the appropriate aqueous-to-organic ratio for each stage.

Hence, this paper aims to examine and develop this process of zinc sulphate recovery from spent pickling liquors via a two step solvent extraction process. Additionally, a simulation of this process is included

---

* Corresponding author. Tel.: +61 3 8344 6682; fax: +61 3 8344 4153.
E-mail address: sandraek@unimelb.edu.au (S.E. Kentish).

0304-386X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.hydromet.2013.11.016

to demonstrate that both high purity and recovery can be achieved using this arrangement.

2. Method

2.1. Experimental

The extractants TBP (Consolidated Chemical Co., purity 99.0%) and D2EHPA (Albright & Wilson Specialties, 97%), were used as supplied and ShellSol 2046 from Shell Chemicals (69 wt.% paraffin, 14 wt.% naphthenes napthtalenes, 17 wt.% aromatics) was used as diluent. Hydrochloric acid (Sharlau, 37 wt.% HCl) and $ZnCl_2$ (AJAX Finechem Pty. Ltd., 95.0%) were used to prepare model solutions while sodium chloride (Chem Supply, 99.0%) was added to adjust total chloride concentration to 5 mol/L, unless otherwise stated. Sodium hydroxide (Chem Supply, 97.0%), di-sodium ethylenediaminetetraacetic acid (EDTA) (Chem Supply, 99.0%), sodium acetate (Chem Supply, 99.0%), glacial acetic acid (Chem Supply, 99.7%), and silver nitrate (MERCK, 99.5%) and were used in titration for sample analysis.

Aqueous phase compositions for experiments using model solutions were determined using titration. 0.05 mol/L EDTA in pH 5.5 acetic acid buffer solution was used to titrate for zinc with xylenol orange used as indicator (Wilson and Wilson, 1960). 0.01 mol/L NaOH was used for acid titration with methyl orange indicator. Chloride concentration was determined by potentiometric titration with 0.02 mol/L $AgNO_3$ using a Metrohm Titrando 809 auto-titrator with a Ag/AgCl electrode and software package Tiamo 1.0.

Shake tests were conducted to obtain the necessary equilibrium isotherms. An orbital-shaker/incubator (Ratek OM15C) was used for consistent mixing at a set temperature. Since TBP and D2EHPA solutions extract water, the organic phase is first contacted with water before use in experiments (Darvishi et al., 2007; Hardy et al., 1964; Mokili and Poitrenaud, 1995; Roddy and Mrochek, 1966; Sainz-Diaz et al., 1996; Sato et al., 1978). 50 vol% TBP in ShellSol 2046 and 25 vol% D2EHPA in ShellSol 2046 was used.

The aqueous and organic phases were mixed in a separating funnel at an aqueous-to-organic (A:O) ratio of unity and preheated to 30 °C in the orbital mixer/incubator for 30 minutes. The mixture was then shaken for an hour at 150 rpm (revolutions per minute) and allowed to stand vertically within the mixer/incubator for a further half an hour to achieve complete phase separation. As the equilibration time for both TBP and D2EHPA extractants are fast (less than 10 minutes; Fletcher et al., 1968; Huang and Juang, 1986; Mishonov et al., 2004; Pereira et al., 2007; Sato et al., 1978), the shaking time used in these experiments is more than sufficient for both phases to equilibrate. The aqueous phase was collected and analysed while the organic phase concentrations were determined via mass balance of the aqueous phase.

In stripping experiments, the organic phase was loaded by contacting the organic phase with an aqueous solution of 1.2 mol/L $ZnCl_2$, 1 mol/L HCl and 5 mol/L total Cl^-, and subsequently stripped at varying aqueous-to-organic (A:O) ratios from 50 mL:15 mL to 50 mL:70 mL at the same conditions as the extraction shake tests. Similar tests were also repeated for scrubbing experiments at unit A:O ratio.

2.2. Modelling

Modelling of the solvent extraction process conducted in this work follows the method outlined by Baes (2001): the aqueous phase activity coefficients were calculated using the Pitzer model (see Tables S1 and S2 in the Supplementary data) while the organic phase activity coefficients were determined with the Hildebrand–Scott model (Table S3). The necessary parameters for both the Pitzer and Hildebrand–Scott models and also the thermodynamic equilibrium constants necessary for the modelling of zinc extraction by TBP (Scheme S1 and Table S4) have been determined in earlier work (Lum et al., 2012; Lum et al., 2013) while that of zinc extraction by D2EHPA were published by Mörters and Bart (2000). For brevity, the relevant equations and methods are not repeated here. The simulations are run using MATLAB® (Mathworks), a commercially available technical computing package.

3. Process development

A generic scheme of the process under study is depicted in Fig. 1.

From Fig. 1, TBP extracts $ZnCl_2$ and, to a lesser extent, HCl. These two extracted species are stripped into a stripping solution (Strip. Soln 1),

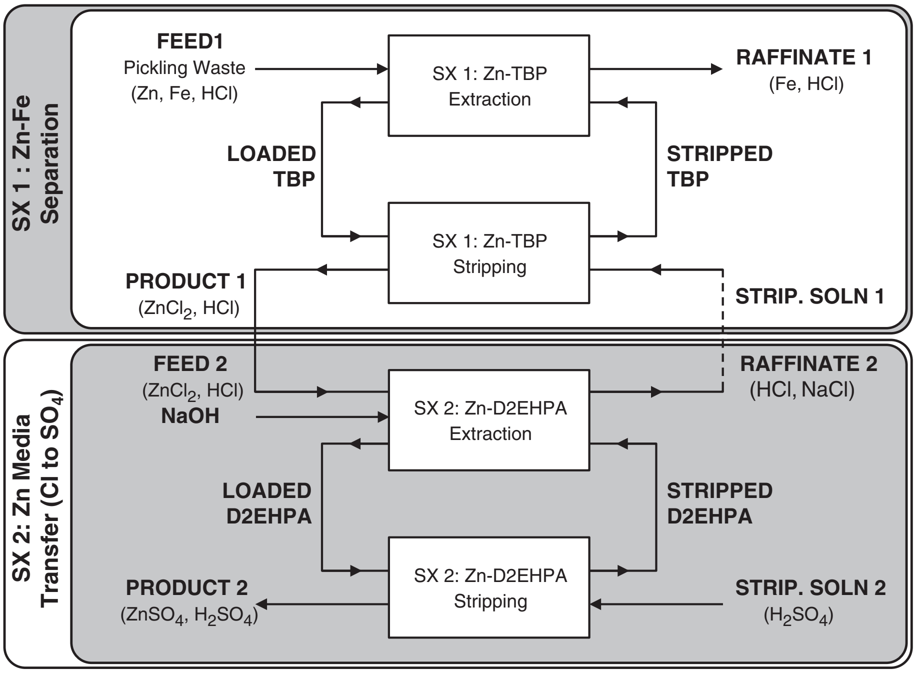

Fig. 1. Block flow diagram of the proposed zinc sulphate recovery process.