Development of an efficient process for the recovery of zinc and iron as value added products from the waste chloride solution

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Manish Kumar Sinha [a,b], Swati Pramanik [a], Sushanta Kumar Sahu [a,*], Lal Bahadur Prasad [b], Manis Kumar Jha [a], Banshi Dhar Pandey [a]

[a] Metal Extraction and Forming Division, CSIR-National Metallurgical Laboratory, Jamshedpur 831007, India
[b] Department of Chemistry, Banaras Hindu University, Varanasi 221005, India

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The present paper deals with the recovery of the Zn(II) and Fe(II)/Fe(III) from the waste chloride solution of steel industry using solvent extraction and precipitation-stripping process for the synthesis of high purity value added products. The extraction of zinc and iron was performed using Cyanex 923. It was observed that Cyanex 923 selectively extracted Zn(II) and Fe(III) from the acidic chloride solution leaving behind Fe(II) in the raffinate. The loaded organic was stripped efficiently using oxalic acid to precipitate Zn(II) as zinc oxalate and Fe(III) was transferred to the aqueous phase as highly soluble ferric oxalate solution while simultaneously regenerating the Cyanex 923. The zinc oxalate was calcined to obtain the high purity zinc oxide (99.9% pure). Further the ferric oxalate solution was reduced by using Fe-powder to get ferrous oxalate, which on calcination yielded pure hematite. The oxalates and oxides were characterized by chemical analysis, XRD and SEM studies to establish the purity and morphology of the as-synthesised products.

1. Introduction

Prior to hot dip galvanizing, steel surface is generally washed or cleaned in order to dissolve the rust products (iron oxides into iron chloride) by dipping it into a hydrochloric acid bath of certain concentration (∼20%). The same acid bath is used continuously till its acidity falls to an unacceptable range (<5%) for further pickling process. Sometimes the same pickling bath is also used periodically for the removal of depleted zinc layers from the old or used galvanised steel. The zinc contamination also comes from the hooks and zigs used for hanging the steel during pickling process. Consequently, in the course of pickling process, large concentration of Zn and Fe (mainly Fe(II)) builds up in the solution. Based on the available reports by various investigators [1–11], the average composition of spent hydrochloric acid pickling solution can be represented as: 10–250 g/L (0.27–6.8 M) HCl, 5–120 g/L (0.076–1.8 M) Zn and 5–200 g/L (0.09–3.6 M) Fe(T). Owing to its acidic nature and high metal content the pickling solution is considered as hazardous for environment and is not endorsed for discarding as such before an appropriate pre-treatment. At the same time such a spent pickling solution has a significant potential to be considered as sec-

ondary resource for Zn and Fe if processed suitably. Although, many processes are available for the treatment of this types of wastes such as spray roasting, electrodialysis, solvent extraction, and precipitation. But most commonly used technique for the processing of spent pickling solution is the precipitation-neutralization process with lime. This process generates huge quantity of sludge which is either disposed as landfill or stored for further processing. The loss of metal values during the precipitation makes this process inappropriate in terms of economic and environmental advantages. Whilst the applications of other processes (spray roasting, electrodialysis, etc.) are associated with some disadvantages like energy inefficiency and production of impure metals values. In recent years various techniques involved in the processing of spent pickling solution have been extensively reviewed [8,12]. However, the use of solvent extraction (SX) method is often recommended over other methods due to its high selectivity and versatility, and ability to produce highly pure products as well as handling of large amount of solutions [13].

For the recovery of Zn(II), Fe(II), Fe(III) and acid from the spent pickle liquor various extractants such as D2EHPA, DBBP, TBP, Cyanex 921, Cyanex 923, Cyanex 301, Cyanex 302, Cyanex 272, Alamine 336, Alamine 308, Aliquat 336, TEHA, and TiOA [1,9,10,13–21], have been comprehensively applied. Above reagents extract Zn(II) and Fe(III) simultaneously from the waste

* Corresponding author.
  E-mail address: sushanta_sk@yahoo.com (S.K. Sahu).

pickle liquor. Zn(II) and Fe(III) present in the organic phase are subsequently separated in the stripping stage.

In the solvent extraction, stripping of loaded metal from the organic phase is conventionally carried out with acid/alkali. From the stripped liquor metal values are then recovered by precipitation/crystallization/electrowinning. However, in precipitation-stripping method stripping and precipitation of loaded metal ions takes place with the help of a stripant containing functional groups which form insoluble salt in the stripped aqueous phase. The precipitates so produced upon decomposition in hydrogen or oxygen atmosphere, are converted to metal/metal oxide powder [22]. For the technological applications of such products, the particles must have uniform shape and close size distribution, low impurity content, etc. Control of particle size is inherently difficult by the usual aqueous precipitation processes [23,24]. It is however, rather easier to control the particle size by varying the precipitation conditions during the precipitation-stripping step [25]. As such the precipitation-stripping process has been predominantly used and reported in the production of rare earth oxalates/carbonates [24,26–30], while fewer reports are available on the production of base metal salts/oxides during the recovery of these metal ions [25,31]. The use of oxalic acid as the precipitation-stripping agent is often preferred due to its ability to form stable chelates with different metal ions generating precursors with a high degree of homogeneity. The availability of oxalic acid at low cost as well makes the production economical. The basic principle or requirement of oxalic acid precipitation-stripping in multi-metal system depends upon the stability constant of the particular metal oxalate and acidity of the solution.

Among several solvent extraction reagents, the use of Cyanex 923 as an extractant for the extractive-recovery of Zn(II) and Fe (III) has been reported by various investigators [8,14,15,21,32–35]. As such Cyanex 923 in spite of being a stable reagent in highly acidic conditions and showing good extraction efficiency, is not recommended for use in the recovery of Zn(II) and Fe(III) from waste pickle liquor due to its poor performance during stripping with hot/cold water, HCl or NaOH solutions [8,14,15]. In view of the above, the present investigation has been carried out with the purpose of extracting zinc and iron from the waste pickle liquor using Cyanex 923 as an extractant in kerosene and separating them by the precipitation-stripping method. This could conveniently be achieved by selective stripping and precipitation of zinc simultaneously from the loaded organic with oxalic acid. Although Fe(III) is also stripped with oxalic acid, but it would remain in the soluble form. While the precipitated zinc oxalate can easily be separated from iron(III) oxalate by filtration, iron(III) oxalate in the filtrate is precipitated as iron(II) oxalate after reduction with iron powder. Subsequently zinc oxalate and iron(II) oxalate have been roasted to produce high pure zinc oxide and hematite, respectively. The products were characterized by chemical analysis, XRD, TG-DTA and SEM-EDS studies.

2. Experimental

2.1. Reagents and materials

Analytical grade reagents such as zinc chloride (ZnCl$_2$, 99%), ferrous chloride (FeCl$_2$·4H$_2$O, 98%), ferric chloride (FeCl$_3$, 98%) and hydrochloric acid (37%) were used to prepare the model solution simulating the average composition of the spent pickle liquor having composition- HCl: 2 M, Zn: 0.76 M, Fe(II): 0.36 M and Fe(III): 0.05 M. Oxalic acid (H$_2$C$_2$O$_4$·2H$_2$O) was used for preparing the stripping solution. All these chemicals/reagents were obtained from Merck, India. Cyanex 923 which is mixture of trialkyl phosphine oxides (alkyl: n-octyl and n-hexyl; Mol. Wt.- 348), was

kindly provided by Cytec Inc., Canada and used without any further purification or pre-equilibration with water. Commercial grade kerosene (Indian Oil Ltd.) was used as the diluent.

2.2. Procedure-solvent extraction and material preparation

Solvent extraction experiments were carried out by shaking equal volumes of the model spent pickle liquor and Cyanex 923 of known concentration in a separating funnel for 30 min, which was found to be sufficient to reach equilibrium. After the phase separation the aqueous and organic phases were separated. Acid concentration in the aqueous phase was determined by potentiometric titration with 1 N NaOH solution, whereas iron was analysed by dichromate method using BDS (barium salt of diphenyl ammine sulfonate) as indicator. The concentration of zinc in the aqueous phase was volumetrically analysed using EDTA in the presence of EBT (Erichrome Black-T) indicator. Precipitation-stripping of Zn(II) was performed after the solvent extraction of Zn(II) and Fe(III) from the aqueous phase. The stripping of loaded Zn(II) and Fe(III) were accomplished by contacting the Cyanex 923 phase with oxalic acid of a known concentration for 30 min. The oxalic acid solution was added dropwise under constant stirring. The stirring was controlled in such a way that a full dispersion of the solution mixture could be attained to avoid the agglomeration of the particles. After mixing the mixture was centrifuged to separate the liquid phases (aqueous ferric oxalate solution and stripped organic solution) from the precipitate (zinc oxalate). The stripped ferric oxalate solution obtained was reduced with iron scraps to form the ferrous oxalate precipitate. After complete reaction, both the products viz. oxalates of zinc and ferrous were filtered by using vacuum filtration then washed with distilled water and stirred in 2-propanol solution for 15 min to remove any organic contaminants. Finally, the washed oxalates were calcined in ceramic crucible for producing zinc oxide and iron oxide powders.

2.3. Characterization of the synthesised products

The oxalate and oxide particles obtained were characterized using various techniques. X-ray powder diffraction (XRD) patterns (Bruker D8-discover) were obtained with Cu Kα (λ = 1.54178 Å) radiation ranging from 2θ = 10–90° at a scanning rate of 2°/min to identify the phases present. The operation voltage and current were kept at 40 kV and 40 mA, respectively. The thermal behaviour of the oxalate powders was investigated in air atmosphere employing thermo-gravimetric (TG) and differential thermal analysis (DTA) (LINSIES GmbH, Germany). The morphologies and particle sizes were also analysed after sputtering with a conductive layer of silver, using a FEI NOVA Nano SEM-430 scanning electron microscope (SEM) with an EDAX attachment for X-ray microanalysis.

3. Results and discussion

3.1. Extraction and separation of zinc and iron from the solution

3.1.1. Solvent extraction of Zn(II) and Fe(III)

In order to optimize the conditions, solvent extraction of Zn(II), Fe(II and III) and HCl from a model waste pickle solution containing 0.76 M Zn, 0.36 M Fe(II), 0.05 M Fe(III) and 2 M HCl was carried out with various concentrations of Cyanex 923 (0.25–1.76 M) in kerosene as diluent, and the results are depicted in Fig. 1. It is clear from the plots that the extraction of different metals followed the order Fe(III) > Zn(II) > HCl. In the entire range of concentration of Cyanex 923 investigated, Fe(III) was completely extracted into to the organic phase, whereas Fe(II) extraction was negligible. The