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Recovery of high value copper and zinc oxide powder from waste brass pickle liquor by solvent extraction

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ABSTRACT

Solvent extraction of Cu and Zn from spent brass pickle liquor has been carried out using LIX 984N as an extractant. Very high difference in $\Delta pH_{1/2}$ value for the two metals during the extraction indicates the ease of separating them under the appropriate conditions. Based on the bench scale results, metals were separated in a continuous mode using a laboratory scale mixer settler unit from the spent brass pickling solution containing 35 kg/m^3 Cu, 30 kg/m^3 Zn, 1.5 kg/m^3 Fe, 0.75 kg/m^3 Cr, 0.03 kg/m^3 Ni and 70 kg/m^3 H_2SO_4 with 30% LIX 984N in kerosene. High copper extraction (99.9%) at the phase ratio (O/A) of 2/1 was obtained at the equilibrium pH of 2.5 in a two-stage counter-current extraction process, leaving behind Zn, Cr and Ni in the raffinate. Zinc from the chromium free solution was then quantitatively extracted in three counter-current extraction stages at pH 5.5 and O/A = 2/1 with negligible co-extraction of nickel. From the respective loaded organic phases, copper and zinc were completely stripped off using 150 kg/m^3 H_2SO_4. The stripped solutions of Cu and Zn were utilized for the synthesis of high pure Cu metal powder and ZnO particles by the hydrothermal reduction/precipitation processes. Copper powder was synthesised in an autoclave at 20 bar H_2 pressure and 423 K in 2 h. On the other hand ZnO powder (4 bar) was prepared from zinc striped solution at pH 12 in an autoclave under autogenous pressure at 423 K in 2 h. The purity and morphology of the as-prepared powders were determined by chemical analysis, XRD and SEM-EDS studies.

1. Introduction

Industrial wastes generated in metallic industries are generally laden with heavy metals. Brass pickle liquor is also a kind of industrial waste generated during cleaning of the brass surface which tends to build up a black coating by prolonged exposure to the air. The cleaning process involves removal of the oxide layer by dipping the material in dilute sulphuric acid bath, which is usually reused quite a few times before its disposal as a waste. As a result the solution is loaded up with pollutant material such as chromium and high concentration of copper and zinc. Due to its environmentally hazardous and acidic nature it cannot be disposed off without pretreatment. The general treatment of this kind of liquid effluent includes the neutralization by lime. However, this process requires a large amount of alkali/lime resulting in the loss of metal values as well. For the disposal of such industrial wastes, alternate options are increasingly being applied which involves the recovery of the heavy metals as value added products by hydrometallurgical methods in recent years. Recovery of heavy metals as valuable products not only reduces the toxicity of the waste to be disposed off but also conserves natural resources in terms of resource recovery from the waste streams (Silva et al., 2005). Thus the processing of brass pickle liquor by hydrometallurgical route will definitely provide economic benefits in terms of recovery of value added products of copper and zinc and mitigate the pollution problem arsing due to conventional disposal of waste brass pickle liquor.

A number of studies have been reported on the recovery of heavy metals from various waste/secondary resources such as pickle liquors, spent electrolytes, industrial effluents, and brass ash leach liquor. (Sinha et al., 2014; Meshram et al., 2013; Nathsarma, 2002). In all these studies solvent extraction plays a major role in producing high pure precursor solution which is used for making high value products of the heavy metals viz., metal powders, metal oxide powders or salts. Recovery of base metals from copper smelter slag by oxidizing leaching and solvent extraction has been reported by Banza et al. (2002). In this study copper from the leach solution was recovered by solvent extraction with LIX 984 whereas, cobalt and zinc were recovered by solvent extraction with D2EHPA. From the separated solutions metals by electrowinning or metal salts by evaporation-crystallization could be prepared. Sahu et al. (2008) have reported the separation of hexavalent chromium and zinc from electroplating effluent by solvent extraction with tri-n-butyl phosphate and selective stripping with dil. sulphuric acid and sodium hydroxide solutions, respectively. Agrawal et al. (2008) have developed a SX-EW (Solvent extraction-Electrowinning)

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process to recover high value copper and nickel powder from the copper bleed solution. Recently, Meshram et al. (2013) have extensively reported the solvothermal synthesis of high value copper powder from copper bleed solution of an Indian copper smelter using Versatic 10 acid as an extractant.

Oxime extractants of LIX series are considered to be among the best reagents for the extraction of base metals because of their performance such as excellent phase separation, low entrainment loss to the raffinate, rapid metal transfer kinetics and high extractive strength. Besides, they do not promote excessive crud formation. The LIX reagents have therefore, been extensively applied for copper extraction in the moderately acidic conditions (Lazarova and Lazarova, 2005). Out of several variants of LIX reagents, LIX 984 (Miguel et al., 1997; Kongolo et al., 2003; Zhuo-yue et al., 2005; Jian-she et al., 2002; Dara and Benamor, 2002), LIX 984N (Lazarova and Lazarova, 2005; Sridhar et al., 2009; Sridhar and Verma, 2011a, 2011b) and LIX

Table 1
Comparative study of present study with the previously reported data on the solvent extraction of Cu–Zn using LIX 984N.

Sources	Composition (kg/m^3)	Key Findings	References
Synthetic nitrate solution	5.0 Cu	Basic study for the SX of Cu at pH 2.0 using different LIX based reagents (5% (v/v)); Extraction trend: LIX 65N < LIX 84N < LIX 984N < LIX 860N-I. Negative ΔG° with LIX 984N indicates the extraction of Cu from nitrate media at low pH values.	Lazarova and Lazarova, 2005
Synthetic sulphate bioleaching solution	10.0 Cu and 20.4 Fe	Achieved high separation factor ($\beta_{Cu/Fe}$) with 10% LIX 984N at pH 1.5, O/A 1; 98.5% Cu extracted along with <20% Fe; Cu stripping: 97.8% along with 30% Fe with 1.5 kg/m^3 H_2SO_4 at O/A = 1:2.	Quing-ming et al., 2008
Sulphate leachate of zinc slag	7.66 Cu, 92.75 Zn and 54.42 Cd	Selective extraction (extraction yield: 87.3%) of Cu with 25% (v/v) LIX 984N at O/A = 3:2, pH 1.7. Zn and Cd separation feasibility tested by D2EHPA, D2EHPA-TBP and HEHEP at pH 2.0	Xie et al., 2008
Synthetic sulphate solution	2.5 Cu in presence of Zn, Fe and Mn	Separation factor calculated at total metal concentration of 2.5 kg/m^3 using 18% (v/v) LIX 984N at O/A = 1, pH 2. Extraction order: Cu(II) > Fe(III) > Mn(II) > Fe(II) > Zn(II) at pH 2. Highest separation factor: $\beta_{Cu/Mn}$ = 37, $\beta_{Cu/Zn}$ = 149, $\beta_{Cu/Fe(III)}$ = 17.70, $\beta_{Cu/Fe(II)}$ = 396 at 1.0 kg/m^3 Cu and 1.5 kg/m^3 of each metal ions.	Asghari et al., 2009
Synthetic ammoniacal/ammonium carbonate medium	3.0 each of Cu and Ni with 60 kg/m^3 ammonium carbonate	Cu and Ni co-extracted using 20% (v/v) LIX 984N in 2-stages at A/O = 1.9:1, pH 9.2; After ammonia scrubbing at pH 7, Ni selectively stripped using 9.8 g/L H_2SO_4 in 3-stages at A/O = 1; Cu stripping with 180 kg/m^3 H_2SO_4 in 2-stages at A/O = 1	Sridhar et al., 2009
Synthetic sulphate solution	0.2 Cu	Examined the synergistic extraction of Cu with Cyanex 301 and LIX 984N. Maximum synergism obtained at 1:1 ratio of Cyanex 301:LIX 984N. Distribution coefficients increased with the initial Cu concentration and temperature. Complete Cu extraction in 2-stages at pH 0.24; 90.65% Cu stripped with 6 M HCl and then it decreases because of formation of easily extractable chlorocomplex.	Fouad, 2009
Synthetic Sulphate solution	0.15 Cu, 0.14 Ni, 0.16 Zn	Cu, Ni and Zn extracted at different pH values using LIX 984N = 0.05 M; Cu: 2-stages at A/O = 5.5:1, pH = 3.5; Ni: 2-stages at A/O = 4:1, pH = 7.3; Zn: 2-stages at A/O = 2:1, pH = 8.8; quantitative stripping of Cu and Ni with 2 M H_2SO_4 and Zn with 3 M H_2SO_4	Sridhar and Verma, 2011a
Polymetallic sea nodules digested in 50% H_2SO_4	0.360 Cu, 0.365 Ni and 0.040 Co	Acid neutralized by alkali, Fe precipitated at pH 4.5 and Co(II) converted to Co(III). Cu & Ni co-extracted with 10% LIX 984N leaving Co(III) in the raffinate at A/O = 1 in 8-contacts. After ammonia scrubbing at pH 4, Ni and Cu selectively stripped using 10 kg/m^3 and 180 kg/m^3 H_2SO_4 in 2-contacts. Experiment also performed with ACORGA M5640.	Sridhar and Verma, 2011b
Nitrate leach solutions of waste PCBs	42.11 Cu, 2.12 Fe, 4.02 Pb, 1.58 Zn and 0.4 Ni	99.7% Cu extracted with 1–4 ppm of Zn, Fe, Pb in 3-stages at O/A = 1.5:1, pH 1.5 using 50% (v/v) LIX 984N; Cu stripping: >97% in 4-stages at O/A = 2:1 with spent electrolyte containing 320 kg/m^3 H_2SO_4 and 30.01 kg/m^3 Cu.	Le et al., 2011
Synthetic sulphate solution (composition similar to the plating wastewater)	1.27 Cu and 1.17 Ni	With 15% (v/v) LIX 984N, 92.9% Cu extracted at pH 4 & O/A = 1:1; 93% Ni extracted with 15% (v/v) LIX 984N at pH 10.5 & O/A = 1:1; Cu stripping: >99.1% with 170 kg/m^3 H_2SO_4 at O/A = 1:2; Ni stripping: 99.3% with 200 kg/m^3 H_2SO_4 at O/A = 1:2	Liqing et al., 2011
Sulphate leach liquors	25–27 Cu, ~30 Fe(T), 1.4–1.9 Zn, 0.06–0.1 Co and 0.02–0.03 Ni	Tested extraction behaviour for Cu with LIX 984N, LIX 612N-LV and Acorga M5640. Acid neutralized by alkali. Only 86% Cu extracted in 2-stages at O/A = 4:1, pH 2.2. Fe co-extracted with Cu in LIX 984N. Extraction trend [with 30% (v/v) solvent]: Acorga M5640 > LIX 612N-LV > LIX 984N.	Ochromowicz and Chmielewski, 2013
Synthetic chloride solution	75.6 Cu, 9.78 Fe, 1.95 Zn, 0.918 Pb, 0.906 Ni, 1.02 Cd, 0.101 Cr, 0.173 Hg, 0.046 Ag, 0.052 As and 0.061 Sb	Fe extraction increased with decreasing Cu extraction. Cu/Fe ratio in the organic solution increased with increasing Cu extraction as Fe extraction decreased. Order of loading capacity of Cu: LIX 984 > LIX612N-LV, XI04003 > LIX84-I [extractants = 40% (v/v)]; optimum conditions for Cu extraction with low Fe co-extraction: A/O = 2:1, pH < 0.5, T = 40 °C.	Lu and Dreisinger, 2013
Waste Brass pickle liquor	35 Cu, 30 Zn, 1.5 Fe, 0.75 Cr, 0.03 Ni and 70 H_2SO_4	Acid and Fe removed by SX and precipitation, respectively before extraction of Cu and Zn. Bench scale results applied in lab scale mixer settler unit. Cu selectively extracted at pH 2.5 in 2-stages at O/A 2/1. After Cr precipitation Zn quantitatively extracted at pH 5.5 in 2-stages at O/A 2/1. Stripped solutions used for hydrothermal synthesis of Cu powder and ZnO particles.	Present study