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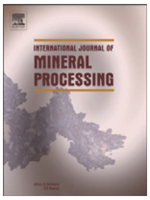

Recovery of manganese and nickel from polymetallic manganese nodule using commercial extractants

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ABSTRACT

The paper describes a process for the recovery of manganese and nickel from the sulfuric acid leach liquor of Indian Ocean manganese nodules using starch as the reductant. The leach liquor contained 22.85 g/L manganese, 6.38 g/L iron, 1.01 g/L copper, 0.023 g/L zinc, 0.09 g/L cobalt and 1.44 g/L nickel. From this leach liquor, Fe was first precipitated out with $Ca(OH)_2$ at pH 3.8 followed by the extraction of copper using LIX 84I. From the almost Fe- and Cu-free leach liquor, Zn was extracted out as an impurity with D2EHPA in kerosene, after which the extraction of Mn was carried out with NaD2EHPA. The extraction efficiency of manganese using NaD2EHPA was 99.93% in 2-stages at A:O ratio of 3:4. The co-extraction of cobalt with manganese was 43 mg/L which was subsequently removed by scrubbing in two stages with $MnSO_4$ solution. The stripping of manganese was achieved with 4% H_2SO_4 in 2-stages at A:O ratio of 1:1. After extraction of Mn, Ni was extracted with NaD2EHPA. The extraction isotherm of nickel reads 2-stages at A:O ratio of 3:2. The co-extraction of cobalt with nickel was 47 mg/L for which the Ni-LO was scrubbed out with $NiSO_4$ solution. The stripping efficiency of nickel was 99.93% with 0.5% H_2SO_4 in 2-stages at A:O ratio of 1:1.

1. Introduction

The manganese nodules deposited on sea bed bearing Mn, Fe, Cu, Co and Ni is considered as an alternative source of the valuable metals for which numerous research programs are being carried out all over the world to recover these metal values in various ways. The hydrometallurgical unit operations such as leaching, precipitation, solvent extraction and electrowinning are being adopted by many researchers for recovery of metal values from manganese nodules. The reduction roast–ammonia leach process for high recovery of iron, manganese, copper, nickel and cobalt values from manganese nodules (Mishra et al., 2011), bioleaching in the presence of the fungus *Aspergillus niger* (Mehta et al., 2010) and sulfuric acid leaching for recovery of rare earth elements (Parhi et al., 2013) were described. Usually in most of the processes, the separation of metal values was carried out by adopting solvent extraction technique after leaching and precipitation.

The recovery of manganese, cobalt and nickel from deep sea manganese nodule was carried out by acid oxidative leaching and solvent extraction (Shen et al., 2007). During leaching, pyrrhotite was used for the effective dissolution of manganese, cobalt and nickel. Cobalt and nickel from the leach solution were precipitated out by adding sodium sulfide and agitating the solution at 50 °C for 2 h followed by filtration; the filtrate was concentrated to obtain manganese sulfate. The Co and Ni precipitate was dissolved in sulfuric acid and from the solution these two metals were separated out using the extractants D2EHPA and PC88A. In another investigation, sulfuric acid was used as the leachant in the presence of activated charcoal for the leaching of poly-metallic nodules (Sridhar and Verma, 2011) and from the leach liquor, manganese and iron were precipitated out as impurities after which copper and nickel underwent co-extraction and selective stripping using the mixture LIX 984N and ACORGA M5640 leaving behind cobalt in solution. From the hydrochloric acid leach liquor of poly-metallic nodules, Cu(II) and Co(II) were extracted with Cyanex 923 followed by the extraction of Ni(II) with Cyanex 301 (Gupta et al., 2003). For the stripping of the metal value from the loaded organic phase, sulfuric acid (0.001 M) was used for the stripping of Cu(II) and Co(II) and 5% NH_4Cl in 75% NH_3 was used for the stripping of Ni(II). From the SO_2-ammoniacal ammonium sulfate leach liquor of a manganese nodule, after removal of Mn, Fe, Cu and Zn, the separation of Co and Ni was carried out using Cyanex 272 (Parhi et al ., 2008) in which the extracted species were CoA_2 and $NiA_2 \cdot HA$.

In the present investigation, the manganese nodule was leached with H_2SO_4 in the presence of starch as the reductant and the leach liquor contained 22.85 g/L manganese, 6.38 g/L iron, 1.01 g/L copper, 0.023 g/L zinc, 0.09 g/L cobalt and 1.44 g/L nickel. Since the Mn and Ni values in the leach liquor were more in comparison to other metal ions, a process was developed for the recovery of these metal ions using the commercial extractants, LIX 84I and D2EHPA as reported in this paper. The commercial extractants LIX 84I (Lu and Dreisinger,

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2013; Panigrahi et al., 2009; Park et al., 2010; Rout and Sarangi, 2013; Tanaka and Alam, 2010), and D2EHPA (Kim et al., 2012; Li et al., 2011; Wang et al., 2013; Vernekar et al., 2013) were used by many authors for the extraction and separation of the metal ions, and these two extractants have been suitably used in the present investigation for process development relating to the separation of above metal ions.

2. Experimental

2.1. Reagents and apparatus

The manganese nodules collected from the Indian Ocean was used for the study.

The commercial extractants, 2-hydroxy-5-nonylacetophenone oxime (LIX 84I) and TOPS-99 which is Di-2 ethyl-hexyl phosphoric acid (D2EHPA) were used as received from Cognis Corporation, USA and Heavy Water Board, Talcher, India, respectively. Distilled kerosene (140–190 °C) was used as the diluent for all the extractants. D2EHPA was neutralized to 80% by mixing it with stoichiometric quantity of standard concentrated NaOH slurry to form a single phase. All other chemicals used were of analytical reagent grade.

The pH of the aqueous phase was measured with a digital ELICO pH meter, model L1 120 provided with a combined glass electrode and pH of the solutions were adjusted to the desired value by adding NaOH/H_2SO_4 solution. The metal concentration in the aqueous phase was estimated by an atomic absorption spectrophotometer (Perkin-Elmer Model A Analyst-200).

2.2. General extraction procedure

All the extraction experiments were carried out at room temperature i.e. ~30 °C. The extraction/stripping experiments were carried out by equilibrating the aqueous and organic phases for 5 min in separating funnels at A:O ratio of 1:1, but in the construction of McCabe–Thiele diagram, the aqueous and organic phases were contacted at different A:O ratio within 1:5 to 5:1 keeping the total volume constant. After complete phase disengagement, the aqueous phase was separated out and the equilibrium pH was measured. The aqueous phase was diluted with 1 M HCl as required and was analyzed for metal values by an atomic absorption spectrophotometer (AAS). The concentration of metal ions in the organic phase was calculated from the difference between the metal ion concentrations in the aqueous phase before and after extraction. As and when required the metal concentrations in the organic phase were determined after filtration through 1PS phase separation paper and stripping an aliquot of it with H_2SO_4 followed by dilution and analysis with AAS.

3. Results and discussions

3.1. Solvent extraction of leach liquor

The leach liquor contained 22.85 g/L manganese, 6.38 g/L iron, 1.01 g/L copper, 0.023 g/L zinc, 0.09 g/L cobalt and 1.44 g/L nickel. Iron was first precipitated out from the solution followed by the separation of other metal ions using solvent extraction.

3.1.1. Precipitation of iron

For the complete precipitation of iron from the leach liquor, the ferrous iron present in the solution was oxidized to ferric state by the addition of 0.5% H_2O_2 followed by the addition of $Ca(OH)_2$ to the solution to precipitate out ferric iron values. The solution was continuously agitated with a mechanical stirrer while adding $Ca(OH)_2$ and the pH of the solution was raised up to 3.8. The solution was filtered with Whatman 42 filter paper and the residue was washed repeatedly with distilled water to free from adhering metal ions. After iron precipitation the leach liquor contained 6 mg/L iron, 22.85 g/L manganese, 0.76 g/L copper, 0.02 g/L zinc, 0.09 g/L cobalt and 1.44 g/L nickel. The precipitation of iron from the solution can be explained by the following equations:

$$Fe_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Fe(OH)_3 + 3CaSO_4 \quad (1)$$

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O \quad (2)$$

$$Fe_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2FeO \cdot OH + 3CaSO_4 + 2H_2O \quad (3)$$

$$2FeO \cdot OH \rightarrow Fe_2O_3 + H_2O \quad (4)$$

3.1.2. Extraction of copper

The leach liquor containing 0.76 g/L Cu along with other metal ions was equilibrated with LIX 84I in kerosene at pH 3.8. The concentration of LIX 84I was varied from 0.5 (0.016 M) to 7.5 vol.% (0.24 M). The extraction of copper with different extractant concentrations was shown in Fig. 1 which indicated an increase in the extraction of copper from 40.42 to 99.87% with an increase in LIX 84I concentration from 0.5 (0.016 M) to 5% (0.162 M) with zero co-extraction of other metal ions.

To enrich the concentration of copper in organic phase, the extraction was carried out in two-counter current stages with 10% LIX 84I at A:O ratio of 6:1 followed by the stripping of loaded organic with 180 g/L sulfuric acid in two-counter current stages at A:O ratio of 1:1. The second stage raffinate containing 2 mg/L Cu indicated 99.73% extraction and the loaded organic contained 4.55 g/L Cu. After stripping the loaded organic with H_2SO_4, the spent organic contained 12 mg/L Cu indicating 99.73% stripping efficiency.

3.1.3. Extraction of zinc

After Fe and Cu removal, the leach liquor contained 6 mg/L Fe, 2 mg/L Cu, 22.85 g/L Mn, 0.02 g/L Zn, 0.09 g/L Co and1.44 g/L Ni from which Zn was extracted using D2EHPA. After extraction of copper, the equilibrium pH of the solution was 3.0. The concentration of D2EHPA was varied in the range of 0.01 to 0.05 M and the A:O phase ratio was kept constant at 1. The plot of extraction of zinc vs. concentration of D2EHPA was shown in Fig. 2. The extraction of zinc increased from 95.78 to 97.42% with an increasing concentration of D2EHPA from 0.01 to 0.05 M with zero co-extraction of other metals. Thus, zinc was extracted from the leach liquor in 2-counter current stages using 0.02 M D2EHPA. After the extraction of zinc, the second stage raffinate

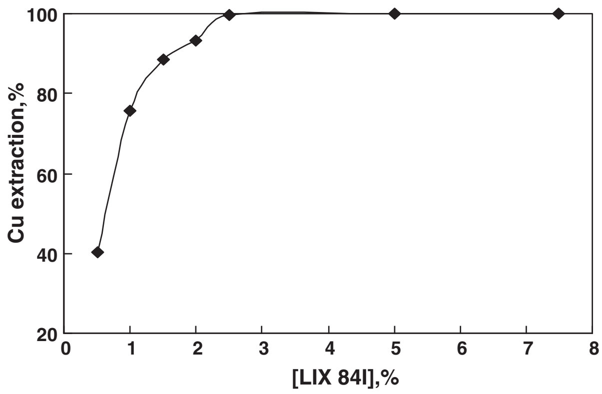

Fig. 1. Effect of [LIX 84I] on extraction of Cu. Experimental conditions: pH 3.8, A:O ratio = 1:1.