

USE OF D2EHPA AS AN EXTRACTANT FOR THE RECOVERY OF Cu, Ni, Co AND Zn FROM AMMONIACAL LEACH LIQUOR OF SEA NODULES

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Extraction studies for copper, nickel, cobalt and zinc from ammoniacal-ammonium carbonate solution of Indian ocean nodules were undertaken using Di-2-ethyl-hexyl-phosphoric acid(D2EHPA). The leach solution was processed for the metal extraction-separation applying the coextraction concept. Besides studying the effect of ammonia concentration, and O/A ratio in different contacts, kinetics of extraction and simulation of continuous extraction were investigated. The simulation experiments carried out on bench scale resulted in the extraction of over 90% cobalt and zinc, and 80-82% copper and nickel from the ocean nodules in a continuous operation with the leach liquor using 0.75M D2EHPA with 20% isodecanol in kerosene.

INTRODUCTION

Polymetallic sea nodules from Indian ocean have recently been recognised as a potential source of metals like copper, nickel, cobalt and manganese. The growing demand of these metals necessitates the exploitation of this resource in the years to come. Ammoniacal leach process[1-4] seems to be advantageous for bringing these metals in solution. A process is being developed at the NML[5] where reductively roasted nodules are leached in ammonia-ammonium carbonate to dissolve selectively Cu, Ni, Co and Zn. The leach liquor containing soluble metal amines could further be treated in a number of ways like precipitation [6], ion exchange [7-8], solvent extraction etc. Of these, solvent extraction is a proven technology for commercial production of several metals, the main advantage being the treatment of complex solutions of the ore processing. A number of patents [9-10] and published information [11-16] elucidate the use of solvent extraction for separating Cu, Ni, and Co from ammoniacal liquors using LIX64N. Other solvents like SME 529 [17] and Versatic 911 [18] were also applied for the separation of these metals from alkaline solution. As LIX64N is mainly designed for Cu extraction, a few newer reagents have recently been brought out with improved properties phasing out the former. Though, LIX 64N possesses excellent properties particularly selectivity for processing ammoniacal leach liquor, its non-availability dictates the need for using an indigenous extractant. Di-2-ethyl-hexyl phosphoric acid (D2EHPA), an indigenously available reagent is thus considered for extraction of the metals from the ammoniacal solution of ocean nodules. The presence of ammonia in leach liquor of nodules may be advantageous due to the deprotonation of the solvent by ammonia

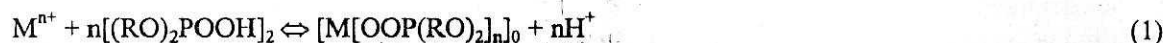
as required[19] for efficient separation. The results of metal extraction from such solution are described using D2EHPA in this paper.

EXPERIMENTAL

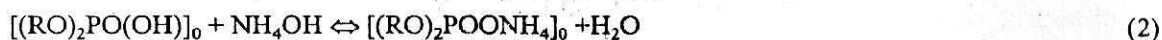
Sea nodules from Indian Ocean were obtained from NIO, Goa and were treated by the process reported elsewhere[20]. The leach liquor generated during ammonia-ammonium carbonate leaching had a typical composition(g/L):Cu-1.8, Ni-2.0, Co-0.206, Zn-0.087, NH₃ 68.3 and CO₂-49.59. All the tests were performed at room temperature. Batch and simulation of continuous tests were performed in glass vessel (600 ml capacity) fitted with baffles while stirring at a regulated speed. A known concentration of D2EHPA diluted in kerosene was used along with isodecanol(ID) as phase modifier. The extracted metals in the organic phase were stripped with 100 g/L H₂SO₄ and analysed in the aqueous phase by AAS. Metal transfer was computed by analysing the aqueous and organic phases, a satisfactory material balance was observed in all the cases. The ammonia and carbondioxide were estimated by acidimetry titration method.

RESULTS AND DISCUSSION

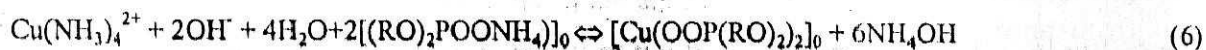
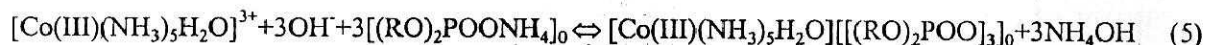
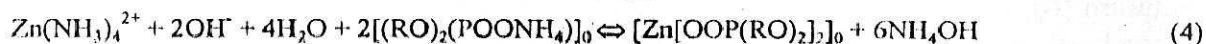
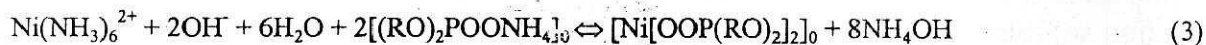
Di-2-ethyl hexyl phosphoric acid (D2EHPA), a phosphatic solvent, may be an important indigenous replacement to the established reagent like LIX 64N. The extraction equation as per Bailes et al [21] is



where Mⁿ⁺ denotes metal ion and o, the organic phase, thus indicating the pH dependence of the extraction of metals. Back extraction or stripping can be achieved by the reverse reaction thereby regenerating the organic phase for recycling. Cook et al [22] proposed the use of D2EHPA in ammonium or sodium form to achieve better pH control in the extraction step.



The leach liquor as obtained by sea nodules processing was ammoniacal, hence the need of conversion of D2EHPA to NH₄ form is obviated. Extraction of copper, nickel, cobalt and zinc from this liquor may be represented as [23]



Extraction studies were initially carried out with the leach solution using 0.5M (16.1% v/v) D2EHPA. The results given in Table I indicate that 0.7g/L Cu, 0.60g/L Ni, 0.116 g/L Co and 0.017g/L Zn was loaded in the solvent during the first contact at O/A 1 and mixing time of 10 min. With the successive contacts of fresh aqueous phase, extraction of these metals in organic phase increased. Thus, in four contacts of organic phase, the amount of metals loaded was found as 0.82g/L Cu, 0.90g/L Ni, 0.296g/L Co, and 0.019g/L Zn. Data plotted in Fig 1 reveal that Zn extraction remained almost steady after first contact whereas Ni extraction became almost steady after second contact. Cu and Co extraction increased even after third contact. Higher magnitude of cobalt extraction at this stage shows the preferential loading of this metal as compared to others.

Table I. Metal extraction in various contacts with actual leach solution.

Aqueous feed(g/L): 1.80 Cu, 2.00 Ni, 0.206 Co, 0.087 Zn, 68.3 NH₃, 49.6 CO₂

Organic feed ; 0.5M D2EHPA, and 10% ID in kerosene.

t = 10 min, No. of contacts = 4, O/A = 1.

No of contacts	Metals in the organic phase g/L				No of contacts	Metals in the organic phase g/L			
	Cu	Ni	Co	Zn		Cu	Ni	Co	Zn
1	0.70	0.60	0.116	0.017	3	0.80	0.85	0.215	0.02
2	0.75	0.70	0.206	0.02	4	0.82	0.90	0.296	0.019

Extraction of metal was studied by varying the ammonia concentration of the aqueous feed and the loading pattern of the solvent in four contacts is given in Table II. It can be seen that extraction of metal is in general favoured at lower ammonia level in the aqueous feed. The amount of different metals extracted from the aqueous feed of 17g/L ammonia was 1.4g/L Cu, 1.50g/L Ni, 0.187g/L Co and 0.050g/L Zn.

Kinetics of metal extraction from the leach liquor was studied for different durations and the results are depicted in Fig 2. The time required for optimum extraction of the metals was 2min at O/A 1 which is ideal for operating a continuous extractor like mixer settler unit. It may be noticed that metal extraction remained constant after 2 min of equilibration

O/A ratio was varied from 1:1 to 4:1 with the aim of extracting maximum amount of metals from the leach solution. Results depicted in Fig 3 show that metal loading increased with increase in O/A ratio, thus maximum loading can be seen at O/A 4 in a single contact. Further increase in O/A ratio was avoided as the phase separation was very difficult due to inseparable third phase formation.

Table II . Metal extraction at different ammonia level in aqueous feed

Aqueous feed(g/L): 1.80 Cu, 2.00 Ni, 0.206 Co, 0.087 Zn

Organic phase: 0.5M D2EHPA and 10%ID in kerosene

t = 10 min, No. of contacts= 4, O/A = 1

NH ₃ in Aq. feed (g/L)	Metals in the organic phase g/L				NH ₃ in Aq. feed (g/L)	Metals in the organic phase g/L			
	Cu	Ni	Co	Zn		Cu	Ni	Co	Zn
17.0	1.359	1.50	0.187	0.05	45.0	1.36	0.97	0.281	0.025
34.0	1.675	1.25	0.268	0.045	68.3	0.82	0.90	0.296	0.019

For the extraction of the metals a continuous extractor may be used. A scheme was thus developed to simulate the counter current extraction as shown in Fig 4. The results of simulated stages of metal for extraction for a mixing time of 2 min at different O/A ratio are given in Table 3. At O/A 1 using 0.75M D2EHPA the 4th stage raffinate contained 0.72g/L Cu, 1.36g/l Ni, 0.052g/L Co, 0.04g/L Zn with the respective metal loading of about 55%, 27%, 76.3% and 50%. When O/A of 2 was used, extraction of cobalt and zinc was 91.8% and 90% and that of Cu and Ni was 82 and 83.7% respectively. The loading pattern of Cu, Ni, Co and Zn in 4 counter current stages at O/A 2 is given in Fig 4. Thus 4 stages are required in a continuous run for high coextraction of these metals. For separation and

recovery, studies are in progress to selectively strip the loaded metals and produce their sulphates/chlorides salts or metal cathode. Data are also being collected to study the NH_3 scrubbing prior to selective stripping. A flow sheet is being developed to separate the metals from the leach liquor of nodules.

CONCLUSIONS

The results show that D2EHPA could be successfully used as an extractant for separation and recovery of Cu, Zn, Co, and Ni from ammoniacal-ammonium carbonate leach liquor of Indian ocean nodule with a maximum extraction at O/A 4 in 4 stages. Faster kinetics of extraction is an advantage for its use in continuous extractor like mixer settler unit to separate these metals. For the separation of these metals from the loaded organic phase selective stripping may be explored besides achieving the separation of these metals in a sequence of preferred extraction, scrubbing and stripping based on pH functionality of the solvent. The metals separated as sulfates/chlorides can be recovered as salts or cathodes.

Table III: Extraction of metals in continuous simulation at different phase ratios

Aqueous feed(g/L): 1.6 Cu, 1.86 Ni, 0.22Co, 0.08Zn, 68.3 NH_3

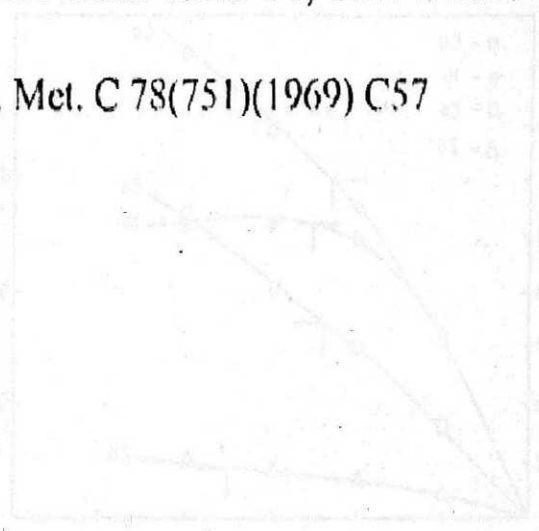
Organic feed: 0.75M D2EHPA and 20% ID in kerosene. t = 5min, No of stages=4

Contact No.	Metal(g/L)				Contact No.	Metal(g/L)			
O/A=1	Cu	Ni	Co	Zn	O/A=2	Cu	Ni	Co	Zn
R1	0.97	1.32	0.09	0.05	R1	0.83	0.75	0.07	0.03
R2	0.90	1.30	0.08	0.04	R2	0.65	0.47	0.04	0.04
R3	0.78	1.32	0.05	0.04	R3	0.40	0.68	0.02	0.01
R4	0.72	1.36	0.05	0.04	R4	0.28	0.32	0.02	0.01
%E in 4th stage	55.0	26.8	76.3	50.0	%E in 4th stage	82.1	83.7	91.8	90.1

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