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Liquid liquidextraction and separation of total rareearth (RE) metals from polymetallic manganese nodule leaching solution

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ABSTRACT:
Thestudyonthesolventextractionforquantitativeandselectiveseparationoftotalrareearthmetalsfromthepolymetallicnoduleleachliquorwasinvestigated.Thetypicalleachliquorbearing0.094g/Ltotalrareearth,0.23g/LMn,0.697g/LCu,0.2g/LFe,0.01g/LCoand0.735g/LNiwassubjectedtotheremovalironcontentbyprecipitationmethodusing$Ca(OH)_2$atpH3.95,priorto solvent extraction of rare earth metals. Three different organo-phosphoric acid reagents (D2EHPA, PC88A, Cyanex 272) wereusedtoascertaintheirperformancesandselectivitytowardstheloadingofrareearthmetalsinpresenceofotherbasemetals.Basedontheresultsofeq.pHeffect,theperformancesofabovethreeextractantsfollowedtheorderas:D2EHPA>PC88A>Cyanex272.To ensure the absence of extraction of base metals (Cu, Co, Ni), the eq. pH of the solution was optimized at the level of 2.21, thoughhigherrareearthmetalextractionefficiencywasobservedathighereq.pHwitheitheroftheextractants.Thecompleteprocessflowdiagram for substantial recovery of total rare earth was developed using D2EHPA. Extraction isotherm plot was constructed atA:O=12:1, 3-stages and pH_e=2.21, using 0.8 mol/L D2EHPA and the predicted condition of this study was further confirmed by6-CyclesCounterCurrentSimulation(CCS)study.Thestrippingoftotalrareearthfromloadedorganicphase(LO)wascondductedusingHClsolution.McCabeThielediagramstudycarriedoutatA:O=1:5using4mol/LHClshowedthatthreetheoreticalstageswereneededforquantitativestrippingoftotalrareearth.Thesubsequentstrippedsolutionresultedthusledtocontaintotalrareearthof5.6g/Lindicatingaveryhighenrichmentoftotalmetalsbysolventextraction(SX)process.

Keywords:totalrareearth(RE)metals;SX;D2EHPA;HCl;deepseanodule

I. INTRODUCTION

Owing to the number of uses and applications in sev-eral electronics (semi/super conductors), medicine, ce-ramics and aerospace engineering sectors[1,2], rare earthmetalsandtheircompoundareofhugedemandinrecentdays. These rare earth metals are being used as novelmaterials with specific functions in advance technologydevelopmentduetotheiruniquespectroscopicandmag-netic properties. The primary rare earth resources likeMonazite, Bastansite[1,3] bear considerable quantity rareelements in which the metal namely, Ce, La, Nd, Y andPrarepresentasthemajorconstituents.Nevertheless,thelow grade minerals such as withered crust also containseveralrareearthmetalslikeNd,Y,Pretc.,althoughto-tal rare earth content is very small. Similarly, low gradeorenamelydeepseanodulecrustfoundinPacificoceanalsoclaimstohavealowquantityofRE(totalrareearth(RE) metal~500–1000 ppm) in addition to the existingother valuable metals i.e. nickel (1.25%–1.5%), copper(1%–1.4%),cobalt(0.2%–0.25%)andmolybdenum(~0.05%)[4,5],whichcanberecoveredbyhydrometallur-gical processing route. Since total rare earth metal concentrationislow,henceasuitabletechnologywasurgedtorecoverandenrichthetotalREcontentfromthedeepseanodules.

Hydrometallurgical process such as leaching[6–8] is avery common method to recover the rare earth metalsfromvariousrareearthmetalbearingsources(primary/secondary)leadingtothedissolutionofsaidmetal(s) into the respective lixiviant phase along with unde-sired other metal/impurities. Thus, the issue is the selectiveaswellasquantitativeseparationofrareearthmetals in presence of other metals/impurities from the subse-quent leaching solution[7]. In hydrometallurgy, the separationprocessesnamelysolventextraction,ionexchangeseparation, supported liquid membrane, adsorption, andprecipitation methods are very familiar while extractingtherareearthmetalsfromnumerousaqueoussolu-tions[9–16]. Among these, solvent extraction (SX) methodhaswiderangeofapplicationinhydrometallurgicalseparation process owing to its great potential on highselectivity, effective separation and high metal enrich-ment[12]. Based on which the separation and purificationof these elements (lanthanides and actinides series) bySXhasgainedconsiderableimportanceinrecentyears[13].

Theorganicextractantssuchasdi-2-ethylhexylphospho-ric acid (DEHPA), PC88A, (EHEHPA), Cyanex 272,Cyanex301,Cyanex302havebeenextensivelyusedforseparationofrareearthmetalsfromleachingsolutions[17–19]. The extractant like D2EHPA/TOPS 99 has awide range of application and becomes more causativeforeffectiveandefficientextractionofrareearthmetalsfrom the various aqueous complex mixture solutions[20].Nevertheless, it is also found as a cost effective reagents ascomparedtootherorgano-phosphorousreagentsandthereby,itisbeingregardedasoneofthebestsuitablecommercialorganicextractantinsolventextractionprocess.

In our previous studies chemical leaching of total REwas carried out using dilute H_2SO_4 [21]. At the optimumleachingcondition,totalREof~0.094g/Lalongwith 0.23g/LMn,0.697g/LCu,0.2g/LFe,0.01g/LCoand0.735 g/L Ni was obtained. The above leach liquor containslowconcentrationoftotalREalongwithothermetalssuchascopper,nickel,cobalt,ironandmanganeseinwhichthelowcontentofironisconsideredastheimpurity. Therefore, after removal of the impurities namelyiron from the leach liquor, the solvent extraction techniquecanbeusedtoseparateandrecovertotalREmetalsselectively. Thus, the final rare earth solution can besubjectedtotheproductionofpurerareearthcompoundswhichisofhighdemandinthecurrentagesfortheinu-meroususes forveryspecificapplications.

As of now, the reported research works related to therecovery of rare earth metals from sea nodules is scanty.Therefore, present research investigation was aimed todescribetheselectiveextractionoftotalREmetalswhichincludes15rareearthmetals(La,Ce,Pr,Nd,Sm,Eu,Gd,Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) from the deep seapolymetallic nodule leach liquor by solvent extractionmethod.InitiallyalmostallironcontentwasremovedBy

Table1Rareearthmetalconcentrationinoriginalseanod-uleleachliquor(mg/L)

NameofelementY	La	Ce	Pr	Nd	Sm	Gd	Eu[M]
	18.6	7.08	16.25	4.26	16.64	5.665.851.55	
Nameofelement	Dy	Ho	Er	Tm	Yb	Lu	
	Tb[M]	6.35	1.84	3.8	0.492.670.4561.95		

1.2Solventextractionprocedure

Equal volume of aqueous and organic phase wereequilibratedfor5min(unlessotherwisespecified) usingseparatingfunnel(60mL)otherthaninMc-CabeThieleplotswhereO:Aratiowasvariedwithintherangeof1:5to5:1whilekeepingthetotalvolumeofbothphasescon-stant. Prior to that pH of the aqueous solutions were adjustedtothedesiredlevelbyadditionofdiluteH_2SO_4or NaOH. After equilibration both the phases are allowedfor phase disengagement followed by separation andequilibriumpHmeasurement.Theaqueoussampleswerediluted totherequirednumberoftimesbydistilled waterand the loaded organic phases were stripped with the 2mol/L HCl (4 times) followed by diluting precipitationroutefollowedbysolventextractionofrareearth metals by investigating with different solvent extractionvariablesusingD2EHPAastheextractant. to the desiredtime in order to determine the concentration of RE metalsaswellasotherbasemetals(Cu,Co,NiandMn)us-ing ICP-AES (JOBIN-YVONJY 38 plus). All the experiments were performed at an ambient temperature(25±5ºC).

The concentration of metal ion in organic phase wascalculated from the difference between the metal con-centration in the aqueous phase before and after extrac-tion. The distribution coefficient (D) and percentage ofextraction (% E) were calculated using Eq. (1) as de-scribed below. The chemical reaction involved on sol-vent extraction of RE metals with extractant can be expressedasgiveninEq.(2).

$(D.\frac{V_{org}}{})$

$E□\frac{V_{aq}}{}□100\%1(D.\frac{V_{org}}{})$

V_{aq}

(1)

1 Materialsandmethods

Reagents

The typical leach liquor obtained after leaching ofdeep sea nodule thus contains the total RE metals 0.094g/L, Mn 0. 23 g/L, Cu 0.697 g/L, Fe 0.2 g/L, Co 0. 01g/LandNi0.735g/L.Table1showstheconcentration ofeach of the RE metal of the original sea nodule leachliquor.Thecommercialacidicorganicextractants namelyD2EHPA,PC88AwereprocuredfromDihalichichemical limited (Japan) while CYANEX-272 was suppliedbyCYTECLTD(USA).Thesereagentswereused withoutmakinganyfurtherpurification.Alltheremainingchemicalsandreagentsusedinthispresentinvestigationareofanalyticalgrade(AR).

$$M_{(aq)}^{+3}+3(HR)_{2(org)} \rightleftharpoons MR_6H_{3(org)}+3H_{(aq)}^{+} \quad (2)$$

Where M=La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er,Tm, Yb, Lu, Y, Th and R=organophosphorousextrac-tant.

II. RESULTSANDDISCUSSION

Precipitationofiron

Theactualleachliquorvolumeof25mLweretakenin100mLbeakersandpHofthesesolutionswereadjustedtovariouspHvalueswithintherange2.0–5.0using10%limeslurry.Thesampleswereheatedona waterbathfor1 h, cooled, filtered and analyzed. From the results asshown in Fig. 1, it can be seen that precipitation of ironwas increased with increase in pH. The total iron wasprecipitatedFe$(OH)_3$anditwasincreasedfromnil(at pH 1.5) to 99.99% (at pH 4.97). Co-precipitation of othermetal ions was observed during precipitation of Fe athigher pH ranges except total/either of the rare earthmetals.However,fromtheaboveplot,selectiveprecipi-tation of Fe can be achieved at pH 3.95 without anyco-precipitationofothermetals.

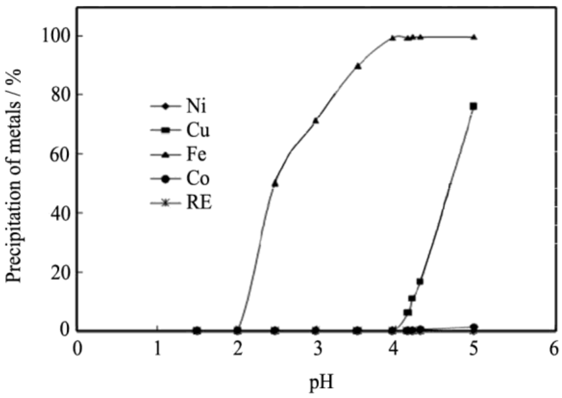


Fig.1PrecipitationofironatdifferentpH

The co-precipitation of total rare earth (RE) metals oreitherofthetrareearthmetalpresentintheleachsolutionwasnotobservedatthestudiedpHrangeswhilestudying the precipitation of iron. Co-precipitation of Cu was niluptopH3.95butincreasedbeyondthatpH.Forexample,at pHvalues of4.15, 4.2,4.3 and4.97,theprecipitation of copper (as Cu$(OH)_2$) was of 6.02%, 10.87%, 16.49%and76.12%.Theamountofcopperprecipitation wassig-nificantly increased with the increasing pH above 4.95,althoughasmallquantityofCuprecipitationcommenceateq.pH4.15asexplainedabove.Thequantityof manganese,inthesolidsphasewasnotobservedsignificantly during precipitation study up to pH 4.3 but it slowly increasedupto5.12%atpH4.97.Manganesewasco-precipitatedasMn$(OH)_2$.

Itwasagainfoundthattheamounts of cobalt and nickel precipitation (as Co$(OH)_2$& Ni$(OH)_2$) was increased dramatically when the pHwas increased beyond 5.0. From this study, it was evi-dent that beyond the pH 3.95, the loss of copper wasfoundtobehighamongrestofthemetalsandtheco-precipitationofthesemetalsfollowstheorderasCu>Mn>Co>Ni. Therefore, it was ascertained that the ironprecipitation Fe$(OH)_3$ was highly selective and almostquantitative at eq. pH 3.95 and this condition was opti-mized for selective removal of total iron from the seanoduleleachsolution.Theaboveobservationswere highly supported by the literatures[22,23] while removingthe base metals impurities from the lateritic and manga-nese nodule sulphate leach liquor as reported by re-searchers.

Based on the above observations, the precipitation ofFe from the leach liquor (bulk quantity) was carried outat an ambient temperature for 1 h. After adding the req-uisite amount of 10% (w/v) lime slurry in order to raisethepHofthesolutionupto3.95.ThisFe-freesolution (filtrate) contained 0.094 g/L total rare earth, ~1.2 mg/L(tracequantity)Fe(99.56%pptn.),0.697g/LCuand 0.23g/LMn,0.01g/LCoand0.735g/LNiwastakentouseforsolventextractionstudy.

Solventextractionoftotalrareearth(RE)metals

Influence of organophosphorousreagents (D2EHPA,PC88A,andCYANEX272)

Three different organic extractants such as D2EHPA,PC88AandCyanex272wereusedforsolventextractionof RE metals. The concentration of either of the extrac-tantwaskeptfixedto0.1mol/LandtheinitialpHofthesolution was increased within 1.0 to 4.85. Accordingly,equilibriumpH(pH$_e$)ofthesolutionwasincreasedintherangeof0.82–2.36,0.89–2.62and0.91–2.98forthecaseof D2EHPA, PC88A and CYANEX-272, respectively.As shown in Fig. 2, the RE metal extraction efficiencywas increased in all the three reagent cases. The REmetal extraction was increased from 2.22% to 97.22%withtheincreaseinpH$_e$from0.82to2.21andthereafter,aplateauvaluewasreached.ThemaximumextractionofRE metals for PC88A and Cyanex 272 were 67.4% and57.68% at the pH$_e$ of 2.62 and 2.98, respectively. On theotherhand,thereisalittleco-extractionofthebasemet-als like copper, Co, Ni and Mn was also observed athigher pH range of the solution i.e. pH$_e \geq 2.32$, pH$_e \geq 2.57$andpH$_e \geq 2.9$incaseofD2EHPA,PC88Aand CYANEX272, respectively and these results are not shown in theabove figure. Based on the results, the performance ofthethreereagentsintermsofREextraction,theycanbeorderedasD2EHPA>PC88A>CYANEX272.Theaboveresultwasfurthersupportedbytheliteratures[20,24-28]andin this regard a comparison Table 2 accomplishing theperformances of organphosphrous reagents while ex-tracting the RE metal(s) from numerous aqueous solu-tionswasprovided.

Fromtheresultsofthepresentstudyandthecompari-sonwiththereportedliteratures(aspresentedinTable2) it was ensured that the usage of D2EHPA for selectiveand quantitative extraction as well as separation of REmetalsfromsulphatesolutionbearingtheotherbase

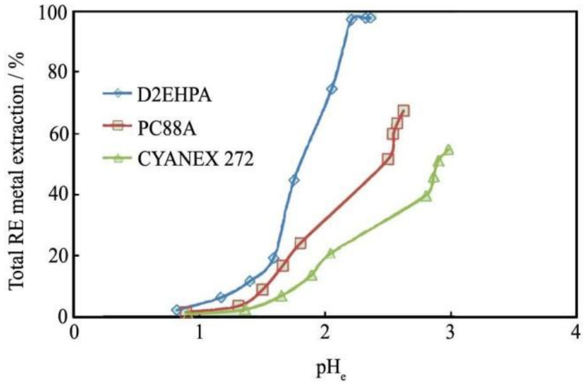


Fig.2Extractionprofileoforganophosphorousreagentsatdif-ferentpH$_e$

Table2Comparisononthe performanceoforgano-phosphorousbasedextractantsforextractionofrareearthmetals

Extractant(s)	Titleofarticles	Remarks	Ref.
D2EHPA,PC88A,CYANEX-272	Liquid-liquidextractionandseparationoftotalrareearth(RE)metalsfromthepolymetallicmanganesenoduleleachsolution	ExtractionoftotalREEusingD2EHPAishighlyselective in presence of other base metals at acidic pHranges and efficient as compared with PC88A andCyanex272	Parhi et al.(PresentWork)
D2EHPA,PC88A	SolventextractionofLa(III)andNd(III)fromnitratesolutionswith2-ethylhexylphosphonicacidmono-2-ethylhexylester	D2EHPA has higher extraction efficiency thanPC88A because of high loading capacity but PC88AwasfoundtobesuitableforselectiveseparationofLaandNdinthisstudy	Kao et al.2006[24]
D2EHPA	SeparationofmajorimpuritiesCe,Pr,Nd,Sm,Al,Ca,FeandZnfromLa using bis(2-ethylhexyl)phosphoric acid (D2EHPA)-impregnatedresininahydrochloricacidmedium	The use of D2EHPA impregnated with resin waspromisingoneffectiveremovalofRREmetaland basemetals	
D2EHPA,PC88A,CYANEX-923	DistributioncoefficientsofLa,Ce,Pr,Nd,andSmonCyanex923-,D2EHPA-,andPC88A-impregnatedresins	Large separation factors and loading of Ce, Pr, Nd,and Sm from La solution was resulted with D2EHPAascomparedtoPC88A,CYANEX-923	Lee et al.(2010)[25]
D2EHPA,HDEHP	Synergisticextractionofrareearthbymixturesof2-ethylhexylphosphoric acid mono-2-ethylhexyl ester and di-(2-ethylhexyl)phosphoricacidfromsulfuricacidmedium	Mixture of D2EHPA, HDEHP showed better energyforquantitativeextraction of ether of metals (Nd/Sm)fromsulphatesolution	Lee et al.(2009)[26]
HEH(EHP),D2EHPA	Processdevelopmentfortherecoveryofhigh-gradelanthanumbysolventextraction	QuantitativeandefficientrecoveryofLaandNdfromchloride solution with organophosphrous reagent (s)wasobserved	Huang et al.(2008)[27]
TOPS99(D2EHPA)	Solventextractionandseparationofrare-earthsfromphosphoricacidsolutionswithTOPS99	Separation of rare earth metals and light rare earthmetals from phosphoric acid solution was achievedusingD2EHPAasthesolventreagent	Moraiset al.(2004)[28]
			Radhikaet al.(2011)[20]

metals like Cu, Co, Mn and Ni at acidic pH ranges wasrational while compared with other organophosporousreagents. Therefore, D2EHPA was chosen as the bestsuitableextractantamongtheusedthreeorgano-phosphrous reagents for the RE metal extraction in thepresentinvestigation.

Influenceofcontacttime

The effect of phase contact time for the extraction oftotal rare earth metals was carried out using 0.1 mol/LD2EHPA at pHe-2.21 (initial pH 4.0) and contact timeranges from 0.5 to 10 min. The results of the extractionof rare earth metal with time are shown in Table 3. Asexpected, the total rare earth extraction showed fast rateand it was maximized up to 97.21% just after 3 min ofcontact time. Thereafter, total RE extraction efficiencyalmost remained unaltered. However, the phase contacttime of 5 min was kept fixed for further experimentations.

InfluenceofequilibriumpH

TheextractionoftotalrareearthmetalsfromdeepseanoduleleachliquorwascarriedoutattheequilibriumpHrange of 0.82 to 2.36 (1.0–4.85). The extraction efficiency of D2EHPA towards the extraction of total REand other base metals at different equilibrium pH aregiveninTable4.ThisshowedthattheextractionoftotalREwasincreasedfrom2.22%to97.2%withincreasein eq. pH of 0.82 to 2.21 and on further increase in eq. pHdoes not affect the RE extraction significantly. The extraction behavior of each of the rare earth metals is alsoshowninFig.3.Fromtheresults,itwasensuredthattheselective extraction of total RE can be obtained at eq.pH≤2.21(pH4.0).Beyondthisrangethecoextractionof Mn, Cu and Ni were observed. With regards to the extraction behavior, each of these RE metals followed asimilarextractiontrend.

Table3ExtractionoftotalREmetalsatdifferentcontacttime

Equilibrium time/min	0.5	1.0	2.0	3.0	4.0	5.0	10.0
Extractionof totalRE/%	54.44	72.9	82.63	97.21	97.24	97.26	97.26

From Eh-pH diagram of lanthanides[29] especially forLa, Nd and Pr (since their concentration is significantlyhighintheinitialleachliquorsascompared tootherRE),they are generally highly stable at acidic pH ranges inaqueousphaseat+3oxidationstate.Thereby,theextractionfollowsthecationexchangemechanismasdescribedin Eq. (2) and the extraction is effective at the abovestudied ranges. Thus, in order to have a clean and selectiveseparationoftotalREthepH$_e$of2.21waschosenasthe optimum condition and it was kept fixed for subsequentstudies.

Table4Extractionofmetalsatdifferent pHlevels

InitialpH	Eq.pH	Mn/%	Cu/%	Co/%	Ni/%	TotalRE/%
1	0.82	0	0	0	0	2.22
1.5	1.17	0	0	0	0	6.31
2	1.4	0	0	0	0	11.64
2.5	1.59	0	0	0	0	19.26
3	1.75	0	0	0	0	44.61
3.5	2.05	0	0	0	0	74.45
4	2.21	0	0	0	0	97.21
4.5	2.32	1.73	1	0	0.14	97.63
4.82	2.36	5.63	4.3	0	0.27	97.71

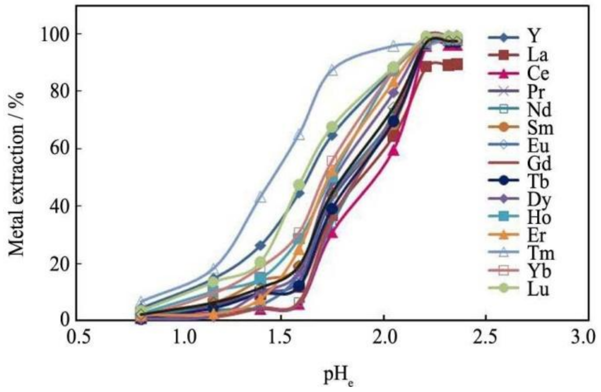


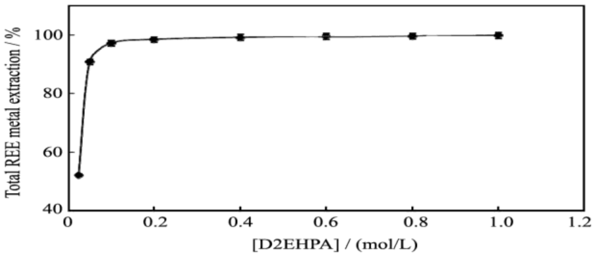
Fig.3Effectofeq.pHonextractionofREmetals

InfluenceofD2EHPAconcentration

The extraction and separation of total REE from theleachliquorwascarriedoutatvariedconcentrationranges(0.25to1.0mol/L)ofD2EHPAwhilekeepingthevalueofphaseratio;A:O=1:1,eq.pH2.21(pH4.0)constant.AsshownintheFig.4,thetotalREextractionwasincreasedfrom52%to99.6%whileincreasingD2EHPA concentration from 0. 25 to 0.8 mol/L. Further increaseinD2EHPAconcentrationhadnotaffectedthe metalex-traction efficiency to a greater extent. In addition, theco-extractionofotherbasemetalswasalsonotobservedatthestudiedD2EHPAconcentrationranges.Thus,fromtheaboveresults0.8mol/LMD2EHPAwasfoundtobeoptimum and suitable for further Mc-Cabe Thiele plotstudies, in order to achieve a high enrichment of totalrareearthmetals.

Extraction isotherm of total rare earth extractionTheextractionisothermwasdeterminedbyvarying the phase ratio of A:O from 15 :1 to 1 :5 at equilibriumpH 2.21, using 0.8 mol/L D2EHPA. The A:Oratiovariationstudywascarriedouttofindouttheotheoreticalnumberofextractionstagesandtheextentofenrichmentof total rare earth metals in loaded organic phase duringextraction.TheMc-CabeThielediagramconstructedforextraction of RE metals in Fig. 5 illustrates that almostallrareearthmetalsofthesolutionwereextractedtoor-ganic phase in two theoretical extraction stages at anA:Oratioof12:1.

To confirm the above Mc-Cabe Thiele predicted condition,atwostagescountercurrentsimulation(CCS)



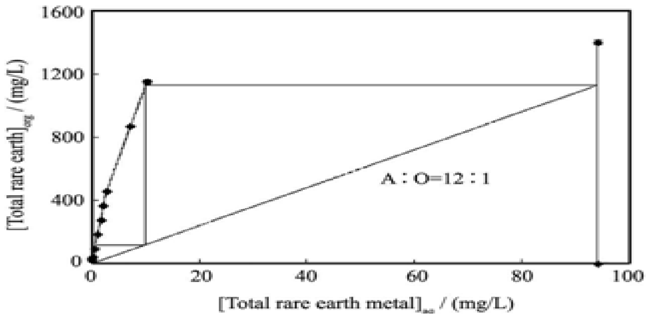


Fig.5Mc-CabeThielediagramforextractionoftotalREmetals

study was conducted up to 6-cycles using 0.8 mol/LD2EHPA at A: O=12 :1and equilibrium pH 2.21.

Theresultedfinalraffinatefromtheabovestudythusreadstocontain ~1.0 mg/L of total rare earth ensuring 99.97%extractionofthetotalrareearthmetal.Theco-extractionsof other base metal (Cu, Co, Ni and Mn) are not foundand were further confirmed by loaded organic analysis.At the above mentioned condition, adequate quantity ofrare earth loaded organic was generated to carry out thestrippingstudies.

InfluenceofcontacttimeonstrippingoftotalREfromloadedorganic(LO)

Asperthereportedliteratures[18,20],HClisanefficientreagent on effective stripping of rare earth metals ascompared to other mineral acids. Moreover, using HCl,therareearthmetalscanbeeasilypreparedbyprecipitationroute.Therefore,reagentHClwasusedforstripping of total rare earth from loaded organic phase. The effectofphasecontacttimeonstrippingoftotalrareearthfromloadedorganicphasewascarriedoutusing1mol/L HCl.As reported in the Table 5, the total RE extraction wasincreased from 19.23% to 74.5% with increase in thephase contact time from 0.5 to 4 min and the strippingequilibrium was attained after 4 min of phase contacttime indicating a very fast back extraction. However,subsequent stripping study was carried out at 5 min ofphasecontacttime.

Stripping of rare earth metals from loaded organicEffectofvaryingconcentrationsofHClintherangeof 0.5–5.0 mol/L were examined for stripping of total rareearth metals from loaded organic phase. The results areshowninFig.6.Strippingefficienciesandphaseseparation of aqueous and organic phases were very good, al-though the quantity of HCl required for quantitativestrippingwascomparativelyhigherthanthestoichiomet-

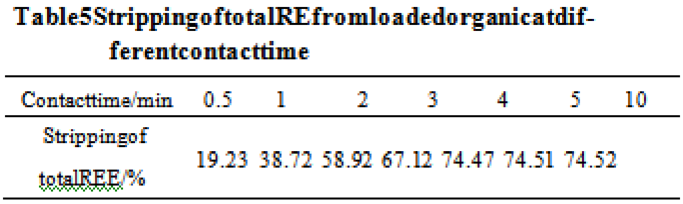


Table5StrippingoftotalREfromloadedorganicatdifferentcontacttime

Contacttime/min	0.5	1	2	3	4	5	10
Strippingof totalREE/%	19.23	38.72	58.92	67.12	74.47	74.51	74.52

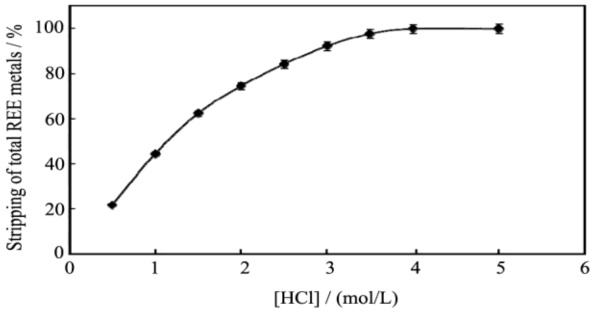


Fig.6EffectofHClconcentrationonstrippingoftotalREfromLO ricamount.ThestrippingoftotalREshowedanincreasingtrend(21.74%to99.77%)withincreasingintheHCl concentration from 0.5 to 4.0 mol/L and beyond whichthestrippingoftotalREalmostremainsunaltered .Therefore,4.0mol/LofHClwaschosenastheoptimum concentration for quantitative stripping of RE from LOand above concentration was kept fixed in subsequentstudies.

Strippingisothermstudies

Tofindoutthenumberofstagesrequiredforstrippingat chosen phase ratio (A:O), stripping isotherm plot fortotal rare earth metal extraction from the loaded organicwas constructed at different phase ratio in the range ofA:O=1:5 to 5: 1, while keeping the total volume of thephases constant. After phase separation, both phaseswereanalyzedformetalconcentration.

As shown in the McCabe-Thiele plot (Fig. 7), morethan 99% of RE metal stripping can be achieved in 3counter-current stages at A:O ratio of 1:5 . To confirm,theaboveprediction,a3-stagecountercurrentsimulation(CCS) study (up to 6 cycles) was performed. This re-sulted a quantitative stripping of total RE metals. Fromthe spent organic analysis result (0.01 g/m^3 of total RE) itwas ensured that a quantitative stripping of total REEfrom the loaded organic phase. Subsequently, that leadstoproducingthestrippedsolutionwhichcontainsabout 5.6 g/L of total REE (stripping efficiency>99.9%), con-firmingtheREenrichmentinthestrippedsolutionupto 5 times as compared to its concentration in the loadedorganic. In addition, overall total RE metal enrichmentwasobtainedas60foldsinthisprocess.

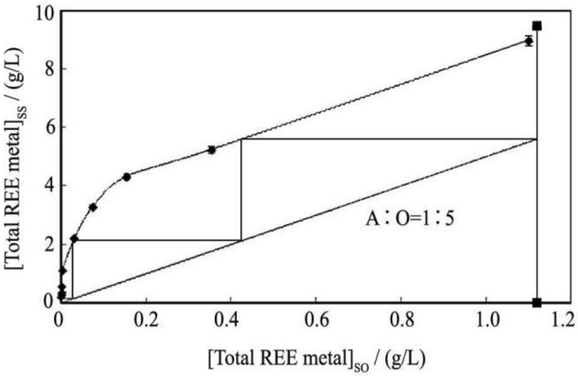


Fig.7Mc-CabeThielediagramonstrippingoftotalREEfromloadedorganic(LO)

III. CONCLUSIONS

The actual sea nodule leach liquor bearing 0.094 g/Ltotalrareearthmetal,0.23g/LMn,0.697g/LCu,0.2g/LFe,0.01g/LCoand0.735g/Lwasmadeironfreeusing $Ca(OH)_2$ solution at pH 3.95 by precipitation method.Co-precipitation of other metal was not observed at theoptimum iron precipitation condition. During screeningof the three organo-phosphorous reagents (D2EHPA,PC88AandCYNEX272)forREextraction study,D2EHPA was found to be suitable for its higher extrac-tion efficiency and selectivity at acidic pH range(s).Theirextractionefficiencyfollowedtheorder asD2EHPA>PC88A>CYANEX272.Aselectiveandcleanseparationvis-à-visahighenrichmentoftotalrareearthfromtheaboveleachingsolutionwasresultedinpresentstudy.Eq.pH,D2EHPAconcentration,andstripsolutionconcentration were found to be critical parameters af-fecting the extraction of total rare earth metal ions. Eq.pH of 2.21 (pH 4.0) was found as suitable and optimumcondition for selective separation of rare earth metalswith~97.21%extractionefficiencyusing0.1mol/LD2HPAatunitphaseratio.Theco-extractionofCu,Co,MnandNiwerenotobservedatthestudiedexperimentalconditions. During extraction isotherm study 0.8 mol/LD2EHPA was kept fixed and thereby, an effective andhigh enrichment (12 times) of rare earth metals to theloaded D2EHPA phase was achieved. During strippingisotherm 4.0 mol/L HCl was chosen as the suitable con-centration and accordingly, the final stripped solutionresulted thus led to bear ~5.6 g/L of total rare earth con-centration. From this study, overall enrichment of totalrareearthwasincreasedto~60timesascomparedtotheREpresentintooriginalleachingsolution.

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