

THE SEPARATION OF SAMARIUM, EUROPIUM AND GADOLINIUM OF HIGH
PURITY BY SOLVENT EXTRACTION

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Extractions of rare earths as a function of DEHPA and aqueous phase hydrochloric acid concentrations have been investigated. The extraction coefficient decreases with increasing concentration of DEHPA and decreases with high concentration of hydrochloric acid in aqueous phase. Selective reextractions of rare earths with different concentrations of hydrochloric acid have been studied. A chemical flowsheet for the separation of Sm, Eu and Gd by 3 cycle extraction with DEHPA-isoparaffin was developed. The purity > 93% of Sm and Eu and purity > 92% of Gd was obtained by liquid-liquid extraction process in laboratory scale.

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INTRODUCTION

The aim of the present work is to develop a commercial liquid-liquid extraction process for the production of pure samarium, europium and gadolinium from rare earths concentrate of NUCLEMON. The commercial organic solvent di(2-ethylhexyl) phosphoric acid (DEHPA) in diluent isoparaffin and rare earths chloride in hydrochloric acid as feed solution were chosen for the process development. Extraction of rare earths by DEHPA from hydrochloric acid solutions has been described by Peppard et.al ⁽¹⁾. DEHPA preferentially extracts rare earths of high atomic number. Extraction of higher atomic number rare earths is favorable at high acid concentration by DEHPA without gel formation ⁽²⁾. The separation and purification of gadolinium and other rare earths have been reported ^(3,4) by solvent extraction process using DEHPA from the feed solution of rare earths in hydrochloric acid solutions. For developing a chemical flowsheet for the separation and purification of samarium, europium and gadolinium on a laboratory scale, basic studies on various extraction parameters, have been investigated. Separation of europium as insoluble EuSO_4 after reduction of Eu^{3+} to Eu^{2+} in Jones Column has been developed.

EXPERIMENTAL PROCEDURES

The feed solutions for the separation process were rare earths chloride (RECl_3), free of Ce, Pr and Nd, supplied by NUCLEMON. DEHPA used was Hostarex PA 216 of Hoechst and Isoparaffina 17/21 of Unipar Química. Batch experiments were performed to determine extraction coefficients ($E^{0/1}$) by equilibrations of equal volumes of RECl_3 solutions and DEHPA-isoparaffin solvents. Reextraction coefficients ($E^{1/0}$) were determined by equilibrating equal volume of loaded organic solvent with varying hydrochloric acid solutions. Preliminary studies on loading of organic solvent, gel formation and efficiency of separation of rare earths were investigated by

simulation technique using cylindrical glass separatory funnels. A laboratory scale mixer-settler of 16 stages, type POLLUX B of France, was used for the separation of rare earths by counter-current extraction process. The stage calculations for the separation of individual rare earths were done by the computer program EXTRACTION written in programming language C using extraction coefficients of rare earths. The control of separation process was done by total rare earths determination by complexometric method, UV-visible spectrophotometry and X-ray energy spectrometry (Kevex system). Europium was separated as insoluble EuSO_4 in inert atmosphere after reduction of Eu^{3+} to Eu^{2+} in Jones Column using 5% amalgamated zinc. The oxide products of samarium, europium and gadolinium were prepared by calcination of respective oxalates of rare earths at 800°C in a muffle furnace. The purity of the products were analysed by inductively Coupled Plasma Spectrometry and Atomic Absorption Spectrometry.

RESULTS AND DISCUSSIONS

Extraction of rare earths by DEHPA

Studies on the extraction of Y, Dy, Tb, Gd, Eu and Sm by DEHPA from the feed solution containing 138 g/l rare earth oxides as supplied by NUCLEMON, showed low $E\%/\Delta$ with 50% DEHPA and the phase separation was very slow. So the feed solution was diluted to 70 g/l rare earth oxides which was similar concentration as used in earlier works at CDTN (3-4). Determinations of $E\%/\Delta$ of Y, Dy, Tb, Gd, Eu and Sm have been done as a function of DEHPA concentration at constant HCl concentrations of 1.20, 1.50 and 1.75 mol/l and the results are shown in table I, table II and table III respectively. Coefficients extraction of Y were greater than unity when DEHPA concentrations were higher than 15% at all concentration of hydrochloric acid solutions studied.

Table I

Extraction coefficients of rare earths as a function of DEHPA concentration in 1.20 mol/l HCl and 70 g/l rare earths oxide

DEHPA Concentration (%)	Y	Dy	Tb	E^{o}/λ Gd	Eu	Sm
15	0.92	0.13	0.046	0.009	0.017	0.0024
20	1.40	0.20	0.075	0.015	0.026	0.0036
25	2.04	0.31	0.10	0.021	-	0.005
30	2.75	0.36	0.15	0.039	0.037	0.017
35	3.89	0.53	0.25	0.041	0.015	0.010

Table II

Extraction coefficients of rare earths as a function of DEHPA concentration in 1.50 mol/l HCl and 70 g/l rare earths oxide

DEHPA Concentration (%)	Y	Dy	Tb	E^{o}/λ Gd	Eu	Sm
15	0.82	0.10	0.041	0.0083	0.014	0.002
20	1.33	0.17	0.073	0.013	0.012	0.0034
25	1.78	0.23	0.092	0.026	0.014	0.0046
30	2.61	0.30	0.13	0.026	0.017	0.0065
35	3.24	0.28	0.14	0.020	0.031	0.005

Table III

Extraction coefficients of rare earths as a function of DEHPA concentration in 1.75 mol/l HCl and 70 g/l rare earths oxide

DEHPA Concentration (%)	Y	Dy	Tb	E^{o}/λ Gd	Eu	Sm
15	0.70	0.10	0.041	0.007	-	0.001
20	1.53	0.21	0.075	0.014	0.018	0.003
25	2.0	0.21	0.075	0.016	0.008	0.004
30	2.48	0.31	0.100	0.024	0.010	0.006
35	3.03	0.46	0.18	0.035	0.037	0.011

The order of E''/a of different rare earths including Yttrium are $Y > Dy > Tb > Gd > Eu > Sm$.

The extraction coefficients of Dy, Tb, Gd, Eu and Sm were lower than unity at all concentrations of DEHPA and hydrochloric acid solutions. The extraction coefficients increased with increasing concentration of DEHPA and decreased with increasing concentration of acid.

The extraction coefficients of Gd, Eu and Sm were in the order of 10^{-2} even at DEHPA concentration $> 25\%$ and those for Y, Dy and Tb were 2-3 order of magnitudes higher than Gd, Eu and Sm.

Based on the extraction characteristics of Y/Dy/Tb and Gd/Eu/Sm, 30% DEHPA and 25% DEHPA and a feed solution of 70 g/l REO in 1.50 mol/l were selected for developing a chemical process for the separation of Gd/Eu/Sm from other rare earths. Preliminary experiments on the separation of Y/Dy/Tb and Gd/Eu/Sm have been carried out in counter current mode using simulation technique. Extractions of Y/Dy/Tb with 30% and 25% DEHPA-isoparaffin from feed solution of 70 g/l REO in 1.50 mol/l HCl solutions in 8 stages with phase ratio of $A/O = 1/2$ demonstrated that Y extracted were 98.8% both by 30% and 25% DEHPA and Gd remained in aqueous raffinate phase were 94.5% and 98.9% respectively. Samarium separated in aqueous raffinate were 98.13% and 99.58% when extractions were carried out with 30% DEHPA and 25% DEHPA respectively.

The results showed that 30% DEHPA did not increase the extraction of Y in comparison to 25% DEHPA and on the other hand coextraction of Gd and Sm was increased. Therefore 25% DEHPA was selected as the solvent concentration for the chemical flowsheet development for the separation of Gd/Eu/Sm from Y/Dy/Tb.

Reextraction of rare earths with HCl

As the extraction of Y, Dy, Gd and Sm by the solvent is an important step, so is the reextraction of these elements in aqueous hydrochloric acid solution for the final preparation of rare earth product either as oxide, carbonate or chloride. The reextraction of rare earths from the loaded solvent has been investigated with different concentrations of hydrochloric acid solutions and the results are shown in table IV.

The reextraction coefficients of Y and Dy are lower than unity in HCl solutions of 1 - 1.75 mol/l and the reextraction coefficients of Gd and Sm are higher than unity in the same concentrations of HCl solutions. At higher HCl concentrations 6 and 8 mol/l, the reextraction coefficients of Y and Dy increased very significantly whereas the reextraction coefficients of Gd and Sm were in the same range of values. For process development 8 mol/l HCl solution was used for the reextraction of Y/Dy/Tb from the loaded solvent.

Table IV

The reextraction coefficient of Y, Dy, Gd and Sm, as a function of hydrochloric acid solution

Concentration of HCl, mol/l	Y	Dy	Gd	Sm
1.00	0.05	0.21	1.03	1.87
1.25	0.09	0.31	1.47	2.11
1.50	0.15	0.47	1.91	3.10
1.75	0.21	0.91	2.81	4.16
6.00	4.63	170.00	39.00	19.00
8.00	11.78	189.00	40.00	19.00

Based on the extraction and reextraction characteristics of Y, Dy, Tb, Gd, Eu and Sm, a chemical flowsheet for the separation Sm, Eu and Gd was developed and is shown in Fig 1.

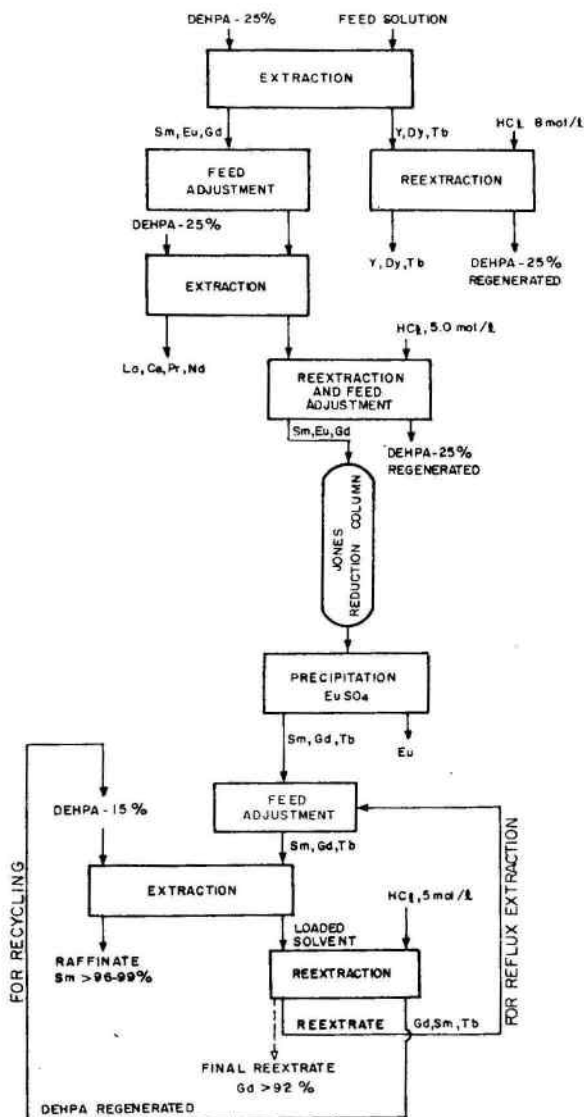


Figure 1 - Flowsheet for separation of Sm, Eu, Gd by solvent extraction.

In the first cycle Sm, Eu and Gd are separated by extraction of Y, Dy and Tb with 25% DEHPA - isoparaffin.

In the second cycle Sm, Eu and Gd are purified from trace amount of Ce, Pr and Nd. Cerium is separated as insoluble CeSO_4 . In the third cycle Sm and Gd are separated with 10% DEHPA-isoparaffin.

Separation of Sm/Eu/Gd from Y/Dy/Tb by first cycle

Studies on the separation of Sm/Eu/Gd from Y/Dy/Tb have been investigated in a mixer-settler. Continuous counter-current extractions of 10 stages with 25% DEHPA-isoparaffin, 70 g/l rare earth oxides in 1.50 mol/l HCl solution as feed solution and with phase ratio of A/O = 1/2 were performed. Reextractions of Y/Dy/Tb were carried out in 6 stages with 8.0 mol/l HCl solution and with phase ratio of O/A = 8/1. For the determination of efficiency of extraction, analytical determination of concentration of Y, Dy, Gd and Sm were done. Yttrium and dysprosium extracted were 98.74% and 78.78% respectively. Small amount of Gd and Sm were coextracted with Y/Dy/Tb and which were 9.08% and 1.49% respectively. Gd and Sm were found in aqueous raffinate phase with 95.92% of Gd and 98.51% of Sm. The profiles of extraction of Y, Dy, Gd and Sm in mixer settler were determined and are shown in table V. Extraction of Y started in the 4th stage and increased sharply at 7th stage and 8th stages. Extraction of Dy increased at 7th stage and then it remained constant after 9th stage.

Coextraction of Gd by the solvent was more than 1 g/l up to 6th stage which decreased to 0.25 g/l at the 10th stage and Sm was extracted in the range of \approx 0.60 g/l up to 6th stage and which decreased to 0.17 g/l at the 10th stage.

Table V

Composition of the extracted rare earths in mixer-settler of counter-current extraction process of 1st cycle

Number of Extraction stages	Elements (g/l)			
	Y ₂₀₃ O ₃	Dy ₂₀₃ O ₃	Gd ₂₀₃ O ₃	Sm ₂₀₃ O ₃
1	0.01	0.04	1.04	0.61
2	0.02	0.33	1.38	0.71
3	0.03	0.74	1.40	0.70
4	0.13	1.33	1.33	0.67
5	0.41	2.15	1.31	0.68
6	1.05	3.05	1.17	0.61
7	2.49	3.70	0.95	0.52
8	4.53	4.05	0.63	0.35
9	7.10	4.35	0.44	0.27
10	8.93	4.50	0.25	0.17

The concentration profiles of Y, Dy, Gd and Sm in mixer settler of the aqueous raffinate phase are shown in table VI. The concentration of Y decreased steeply in 3rd stage when the Y was extracted most favorably and trace level of Y was found in 6th stage and the subsequent stages.

Table VI

Composition of the aqueous raffinate phase rare earths in mixer settler of counter-current extraction process of 1st cycle

Number of extraction stages	Elements (g/l)			
	Y ₂ O ₃	Er ₂ O ₃	Gd ₂ O ₃	Sm ₂ O ₃
1	11.92	6.67	16.63	27.64
2	8.50	8.44	17.59	26.87
3	4.47	8.37	18.02	25.91
4	1.89	7.11	19.00	25.12
5	0.72	5.11	18.74	24.92
6	0.24	3.55	18.63	24.55
7	0.05	2.36	18.68	24.10
8	0.03	1.61	18.71	23.66
9	N.D.	1.04	17.93	23.75
10	N.D.	0.71	16.13	23.14

The concentration of Er was found constant up to 3rd stage and afterwards started decreasing and in the 10th stage it was 0.71 g/l. The concentrations of Gd and Sm slightly decreased in the 1st stage and then increased with the increasing number stages.

Purification of Sm/Eu/Gd from Ce/Pr/Nd by second cycle

The rare earths chloride solutions supplied by NUCLEMON contain 2-5% light rare earths Ce, Pr and Nd which are accompanied the fraction Sm/Eu/Gd in the first extraction cycle. The separation of Ce/Pr/Nd from Sm/Eu/Gd has been carried out by second extraction cycle. Sm/Eu/Gd is extracted by DEHPA, leaving Ce/Pr/Nd in aqueous raffinate phase. The continuous counter-current extraction and reextraction were carried out in a mixer settler to purify Sm/Eu/Gd from trace Ce/Pr/Nd. Extractions of 4 stages with 25% DEHPA and 20 g/l rare earth oxides in 0.25 mol/l HCl and phase ratio of A/B = 1.0/1.5 were performed. Reextractions of Sm/Eu/Gd from organic solvent were carried out in 6 stages with 5.0 mol/l HCl and

phase ratio of O/A = 8/1. Chemical analysis of the separated Sm/Eu/Gd showed that it was free from Ce, Pr and Nd.

Separation of Eu by reduction and precipitation

The separation of europium has been investigated by reduction and precipitation method using Jones Column and sulphuric acid. Eu^{3+} is readily reduced to Eu^{2+} by elemental zinc and the separation of insoluble europous sulphate by sulphuric acid solution has been reported by McCoy ^(19,20). The feed solutions used in the present studies were the separated Sm/Eu/Gd fraction as mentioned in earlier section. The separation of Eu is being carried out using a feed solution containing rare earths solution of 161.3 g/l oxides in 0.05 mol/l HCl solution. Eu^{3+} was reduced to Eu^{2+} in Jones Column, containing 5% amalgamated zinc of 20-30 mesh and precipitating EuSO_4 with 1.0 mol/l H_2SO_4 solution in inert atmosphere of CO_2 .

Pure europium oxide was prepared after dissolution of EuSO_4 , and precipitating as oxalate and calcining at 800°C . The purity of Eu_2O_3 varied from 96% to 98.23%.

Separation of Sm and Gd by third cycle

Samarium and gadolinium were separated by third extraction cycle using 15% DEHPA-isoparaffin and feed solution prepared from the filtrate of Eu separation process. The feed solution was prepared via precipitation of rare earths carbonate and then redissolution in hydrochloric acid. Separations of Sm and Gd were carried out by reflux extraction technique ⁽²¹⁾. Gadolinium was preferentially extracted by solvent, leaving pure samarium in aqueous raffinate phase. A minor part of Sm and other trace heavy rare earths were coextracted with Gd and they were reextracted with HCl and recycled as the feed solution for further separation of Sm.

The concentration of feed solution was varied in each reflux extraction in order to extract mainly Gd and trace heavy rare earths and maintaining aqueous phase acidity constant of 0.40 mol/l HCl. Ten stages of extraction with 15% DEHPA, with phase ratio of A/O = 1.0/1.2 and 6 stages of reextraction with 5.0 mol/l HCl and phase ratio of O/A = 8/1 were used. The extraction of Gd by solvent was > 99.5% in each reflux extraction cycle and the recovery of Sm in aqueous raffinate solution was from 55% to 65% in relation to the Sm in feed solution. In the initial stage of the extraction process, the coextraction of Sm with Gd was 40% and which decreased to < 1% in the final stage of reflux extraction. The product purity of Sm was > 99% up to four reflux extraction process and subsequently decreased to < 95% with greater number of reflux extraction. The recovery of Sm in a raffinate solution was 87% in relation to the initial feed solution. The product purity of Sm varied from > 99% to 96%. The recovery of Gd was > 99.5% and the purity of Gd > 92.34% was obtained. Gadolinium was further purified by batch extraction process with 25% DEHPA using feed solution of 10 g/l in 1.0 mol/l HCl and selective reextraction of Gd by hydrochloric acid solutions. The purity of Gd obtained was 96.53%. The products of Sm, Eu and Gd were analysed for trace rare earths and other impurities by inductively coupled plasma spectrometry (ICP) and energy dependent X-ray fluorescent spectrometry (KEVEX) the analytical results are shown in table VII.

Table VII

The analytical results of Samarium, Europium and Gadolinium products by ICP and Kevex

Elements (%)	Rare Earths Product		
	Samarium	Europium	Gadolinium
Sm ₂ O ₃	99,17	2,16	1,43
Eu ₂ O ₃	0,069	98,2	1,44
Gd ₂ O ₃	0,473	0,27	96,72
CeO ₂	< 0,005	< 0,005	0,033
La ₂ O ₃	0,002	< 0,002	0,079
Nd ₂ O ₃	0,06	0,02	0,07
Y ₂ O ₃	0,005	< 0,005	0,084
CaO	< 0,01	< 0,01	< 0,01
Na ₂ O	0,077	0,098	0,032
Fe ₂ O ₃	< 0,02	< 0,02	< 0,02
ThO ₂	< 0,005	< 0,005	< 0,005
ZnO	0,018	0,0154	0,0057
GdO	< 0,07	< 0,07	< 0,07
NiO	< 0,02	< 0,02	< 0,02

The flowsheet developed by the organic solvent DEMPA-isoparaffin using the rare earth chloride as feed solution has demonstrated that > 98% Sm and Eu and > 92% Gd, can be separated in laboratory scale. Samarium product obtained is of permanent magnet grade. For the separation of nuclear grade Gd (99,9%) and phosphor grade Eu (99,9999%), special purification process is necessary.

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