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**SOLVENT EXTRACTION SEPARATION OF NEODYMIUM AND PROMETHIUM
USING DI(2-ETHYL-HEXYL)ORTHOPHOSPHORIC ACID AS EXTRACTANT**

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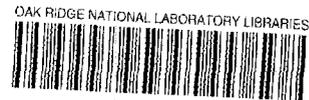
SOLVENT EXTRACTION SEPARATION OF NEODYMIUM AND PROMETHIUM
USING DI(2-ETHYL-HEXYL)ORTHOPHOSPHORIC ACID AS EXTRACTANT

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ABSTRACT

A multistage continuous solvent extraction process using di(2-ethyl-hexyl)orthophosphoric acid (D2EHPA) as an extractant has been developed for the fractionation of the rare earths. The process was developed particularly for the separation of fission neodymium and promethium.

To obtain a significant production rate with D2EHPA requires that the variation in the distribution coefficient of the solute from stage to stage (due to loading effect and pH changes) be controlled within operable limits. This can be done by using a high concentration organic phase (1 molar) and high acid aqueous phase (0.74 molar). With organic phase loading to 24% the variation in K_d does not exceed a factor of 2.

Separation factors using toluene diluent and nitric acid aqueous phase were about 1.7, but the K_d 's were too low for a high production rate at reasonable organic flow. With Amsco as a diluent, the separation factors were still ~ 1.7 , but the K_d 's were much higher.

In the pilot-plant scale demonstration, good process stability and near theoretical separation were obtained in an 11-stage mixer-settler.

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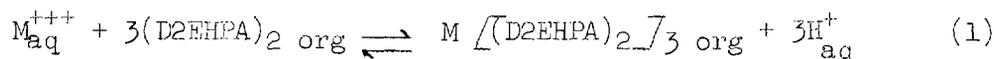
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1.0 INTRODUCTION

The long-lived fission products are separated in the Fission Products Development Laboratory at Oak Ridge National Laboratory (1) from solutions remaining after the reclaiming of uranium and plutonium from irradiated fuel elements. In the fission products recovery process, the rare earth elements are separated by precipitation. It is of great interest to isolate promethium from that fraction. The purpose of this work was to determine the effectiveness of a fractional solvent extraction process, using di(2-ethyl-hexyl)orthophosphoric acid (D2EHPA) in Amsco* as the extractant, as a means of fractionating the rare earths.

2.0 THEORETICAL

The use of D2EHPA for the fractional solvent extraction of lanthanides has been studied by Peppard and co-workers (2,3,4). They have shown that D2EHPA exists largely as a dimer in the organic phase and that each triply charged lanthanide ion in the organic phase is associated with three of these dimers. From this work it is concluded that D2EHPA dissolved in an inert diluent reacts as follows:



where M^{+++} is the extracted lanthanide ion and the subscripts "aq" and "org" refer to the aqueous and organic phases, respectively.

From Equation (1) can be derived the distribution coefficient (K_d) of the lanthanides:

$$K_d = K_{eq} \frac{\left[(D2EHPA)_2 \right]_3}{\left[H^+ \right]^3} \quad (2)$$

This shows that the value of the K_d varies inversely with the cube of the free (unreacted) D2EHPA concentration and directly with the cube of the hydrogen ion concentration. Hence the K_d values depend on how much the organic phase has been loaded -- not only because of the effect of varying the free D2EHPA concentration, but also because of the variation of the concentration of hydrogen ions which are liberated by the transport of solute into the organic phase.

To avoid variation of the K_d with pH in the different stages of a fractional solvent extraction system operating with D2EHPA, it is desirable to have a relatively high acid concentration in the aqueous phase. It is also advantageous to limit the organic loading to avoid excessive depression of the distribution coefficients.

*Amsco is a diluent consisting of a petroleum fraction boiling from 125-182°C.

To operate a fractional solvent extraction cascade successfully, it is necessary that the expressions* $\frac{(K_d O)}{(A + F)}$ and $\frac{(K_d O)}{(A)}$, which relate the K_d and the organic, aqueous, and feed flows in the extraction and scrubbing sections, respectively, be > 1 for the component which is to be recovered in the extract and < 1 for the component in the raffinate. On the other hand, the enrichment of a component in the organic phase is proportional to the value of the two expressions above, so that the larger the difference between the K_d 's of the two components, the better the separation.

Peppard (2) has reported that in the extraction of the lanthanides from aqueous HCl into a solution of D2EHPA, with toluene as a diluent, a plot of $\log K_d$ vs the atomic number Z is a straight line of positive slope corresponding to an average value of the separation factor (ratio of $K_Z + 1$ to K_Z) of 2.5. Thus it should be possible to separate promethium and neodymium from fission products by an appropriate fractional solvent system. The purpose of the work which is reported here was to investigate such a system.

3.0 EXPERIMENTAL

Experimental work included small-scale operations in the laboratory and intermediate-scale operations in a mixer-settler cascade.

3.1 Laboratory Scale

Several experiments were performed to determine values of the separation factor, α , as a function of the characteristics of both the organic and the aqueous phases. The K_d 's were determined by shaking 25-ml samples of organic phase with 25 ml of aqueous phase.

Promethium-147 (β -active, $t_{1/2} = 2.6$ years) and Nd^{147} (β - γ -active, $t_{1/2} = 11.6$ days) were used as tracers so that counting techniques could be used to determine the concentrations of the solutes. Promethium-147 was counted with a Geiger tube, and Nd^{147} with a gamma scintillation counter.

3.1.1 Data and Discussion

The results obtained in tracer-level scale in these preliminary assays are shown in the following table.

*Where A = Aqueous volume
F = Feed volume
O = Organic flow rate

Solvent	Molarity	Diluent	Aqueous	K_d (Nd)	K_d (Pm)	α
Purified D2EHPA*	0.75	Toluene	0.5 <u>M</u> HCl	0.015	0.043	2.85
" "	0.75	"	0.5 <u>M</u> HNO ₃	0.029	0.059	2.03
Unpurified D2EHPA	0.75	"	0.5 " "	0.037	0.066	1.77
" "	0.75	Amsco	0.5 " "	1.59	2.78	1.74
" "	1.00	"	0.5 " "	2.39	4.24	1.77
" "	1.00	"	0.7 " "	0.915	1.46	1.60
" "	1.00	"	0.5 <u>M</u> HCl	2.49	4.41	1.77

The K_d for Nd and Pm using purified D2EHPA in toluene is very low; the separation factor reaches the value of 2.85. With impure D2EHPA in toluene the K_d 's are higher although still very low; the separation factor, on the other hand, is reduced to 1.77. The use of Amsco as a diluent instead of toluene raises the K_d values without reducing the value of α below 1.74.

For the same acidity of the aqueous solution when using hydrochloric acid, the results were not the same as those obtained with nitric acid in the case of purified D2EHPA in toluene; but the difference disappeared when commercial D2EHPA in Amsco was used.

As was to be expected from Equation (2), the lower the pH, the lower the value of K_d ; but it was also found that the separation factor decreased with decreasing pH.

The behavior of gross amounts of Nd is presented in the following table. The data correspond to a total of 11 g/l of Nd and 1.2 g/l of Sm in the combined phases. Samarium usually accompanies Nd and Pm in the rare-earth fission product fraction from which the Pm can then be

*Purified D2EHPA was used in some of the experiments. The purification was carried out by liquid-liquid extraction to separate the mono- and di-ester. A 25-ml sample of commercial D2EHPA was added to a mixture of 75 ml of diethyl ether and 75 ml of ethylene glycol. Following a 15-minute period of agitation, the two samples were separated. The ether phase containing the di-ester was shaken again with a new 75-ml fraction of glycol; the operation was repeated five times. The ether phase was then evaporated at room temperature, leaving the purified D2EHPA. To determine purity, the commercial and purified D2EHPA were titrated with 0.01 M sodium hydroxide (5). The purified product was found to be 99.2% di-ester.

separated. The calculated* extraction of Sm into the organic shows the separation to be almost quantitative.

Organic-Aqueous Ratio	Acidity (M HNO ₃)	K _d Neodymium
1	0.48	2.01
1	0.64	0.97
1	0.70	0.72
1	0.82	0.42
1	0.96	0.32

3.2 Intermediate Scale

Several experiments have been carried out in a mixer-settler cascade to obtain a flow sheet of the separation of Nd from Pm. In testing the flow sheet, the mixer-settlers were operated at the required flow rates of feed, aqueous, and organic solutions.

For tests made on a laboratory scale, radioactive tracers of Nd¹⁴⁷ and Pm¹⁴⁷ were added to the feed, and counting techniques were used to determine the K_d's of the solute.

Samples of the effluent streams were taken in order to determine when steady state was reached; then samples were taken of both phases of alternate stages throughout the mixer-settler. These stage samples were counted and the solute concentrations calculated by converting counting rate to concentration. The pH of the aqueous phase was also determined.

3.21 Equipment

The mixer-settler cascades which were used in these experiments contained 11 stages and measured 20" x 8" x 8". The maximum flow capacity for these mixer-settlers was approximately 2 liters/hour each for the organic and aqueous phases. These units were miniature ORNL-designed "pump-mix" mixer-settlers (6). The pumping action of the impellers in the mixing chambers automatically maintains the organic-aqueous interface at a fixed level.

The flow rates were controlled by suitable metering pumps.

3.22 Process

The feed solution containing 57 g Nd/l and 15 g Sm/l was fed at the rate of 70 ml/hour into the stage-4 mixer. The feed solution also

*Since $\frac{K_d(\text{Sm})}{K_d(\text{Pm})} \approx \frac{K_d(\text{Pm})}{K_d(\text{Nd})} \approx 1.7$

contained about 3 mc Nd¹⁴⁷/1 and 15 mc Pm¹⁴⁷/1 as tracers. The organic stream contained 1 M D2EHPA in Amsco and entered the stage-1 mixer at the rate of 1000 ml/hour.

The aqueous stream to the stage-11 mixer consisted of 0.74 M nitric acid entering at a rate of 1000 ml/hour.

The organic stream was stripped prior to re-use by countercurrent extraction throughout 11 mixer-settler stages by 2.0 M nitric acid at a rate of 500 ml/hour. The results show the decontamination to be almost quantitative.

3.23 Data and Discussion

While operating the cascade at this throughput, it was found that the equilibrium between the aqueous and the organic phases was not reached in any of the stages. In order to improve the efficiency, the speed of the impellers was increased and it was found that equilibrium could be reached at a stirrer speed of 900 rpm. However, the interfaces were difficult to control at high stirrer speeds, and the agitation was so fast that the liquid was sprayed out of the mixing chambers. To avoid these effects, an additional 4-blade impeller was fitted on the end of each shaft, and the original pumping holes were plugged. This arrangement improved the mixing in the bottom of the mixer chambers, and maintained the liquid surface of the stirred mixture within the appropriate level limits, thereby avoiding spray contamination. It also controlled the interface at the required level. Thus the mixers were running at a speed of 900 rpm and the efficiency (the ratio between the K_d found in the particular stage and the K_d obtained by shaking together both phases to equilibrium) reached an average value of 97% in the stages 1 to 10. The efficiency of the 11th stage was found to be less than 60% under these conditions; to improve it, the size of the port between the 11th mixer and the 11th settler was reduced 50%, and the entrance of the aqueous stream was moved to the top of the mixer chamber. With this arrangement an efficiency of approximately 85% was reached in the stage in question.

Under the cited conditions, several runs were carried out employing the double-tracer technique to study the cascade flow sheet. The cascade performance is summarized below.

Stage	Normality of Aqueous Phase	K_d (Nd)	K_d (Pm)	Separation Factor (α)
1	0.70	0.599	0.963	1.608
3	0.67	0.598	0.973	1.601
5	0.68	0.718	1.160	1.615
7	0.70	0.748	1.196	1.600
9	0.72	0.827	1.296	1.567
11	0.73	1.076	1.461	1.357

The Nd and Pm contents of the organic and aqueous streams leaving the mixer-settlers showed 4.65% of the Nd and 56.27% of the Pm in the organic phase, and 95.35% of the Nd and 43.73% of the Pm in the aqueous phase. The Nd cascade profile has been plotted in Figure 1.

The separation factor reached a value of ~ 1.60 in the stages 1 to 10, which agrees with the laboratory data previously obtained. The value of α was lower in stage 11, as expected from the low stage efficiency.

The acidity profile was consistent with the mechanism of the extraction and its small variation resulted in a consistency of the K_d 's along the cascade.

Since the split of Nd was 95.35%, and the recovery of Pm was 56.27%, the Nd decontamination factor (defined as the ratio

$$\frac{\text{Conc. Pm in Extractant} / \text{Conc. Nd in Extractant}}{\text{Conc. Pm in Feed} / \text{Conc. Nd in Feed}}$$

was 11.83.

The highest loading in the organic phase occurs in the stream leaving the feed stage, and it represents a loading of D2EHPA of about 24%. In the last stages the loading is lower, which explains the slight increase in the K_d 's despite the higher acidity.

4.0 CONCLUSIONS

1. The use of Amsco as a diluent for commercial D2EHPA to separate Pm and Nd raises the K_d 's to practical values, but the separation factor is 30% lower than that reported in the literature when using toluene as a diluent for purified D2EHPA.
2. An average stage separation factor of 1.60 has been found in the operation of an 11-stage fractional solvent extraction system using 1 M D2EHPA in Amsco as the organic phase and 0.74 M HNO_3 as the aqueous, and working with a maximum extractant loading of 24%.
3. Under the conditions above, an Nd split of 95.35% was obtained with a Pm recovery of 56.27%. The Nd decontamination factor was 11.83.
4. The 1.60 value of the separation factor compared with the value of 1.96 reported in the bibliography when using TBP as an extractant makes less attractive the use of D2EHPA to fractionate the lanthanides under the conditions studied.
5. As the use of different D2EHPA diluents has been found of great importance in the behavior of this solvent, a careful study of the variation of the D2EHPA properties with the diluent is suggested if further work is to be done.

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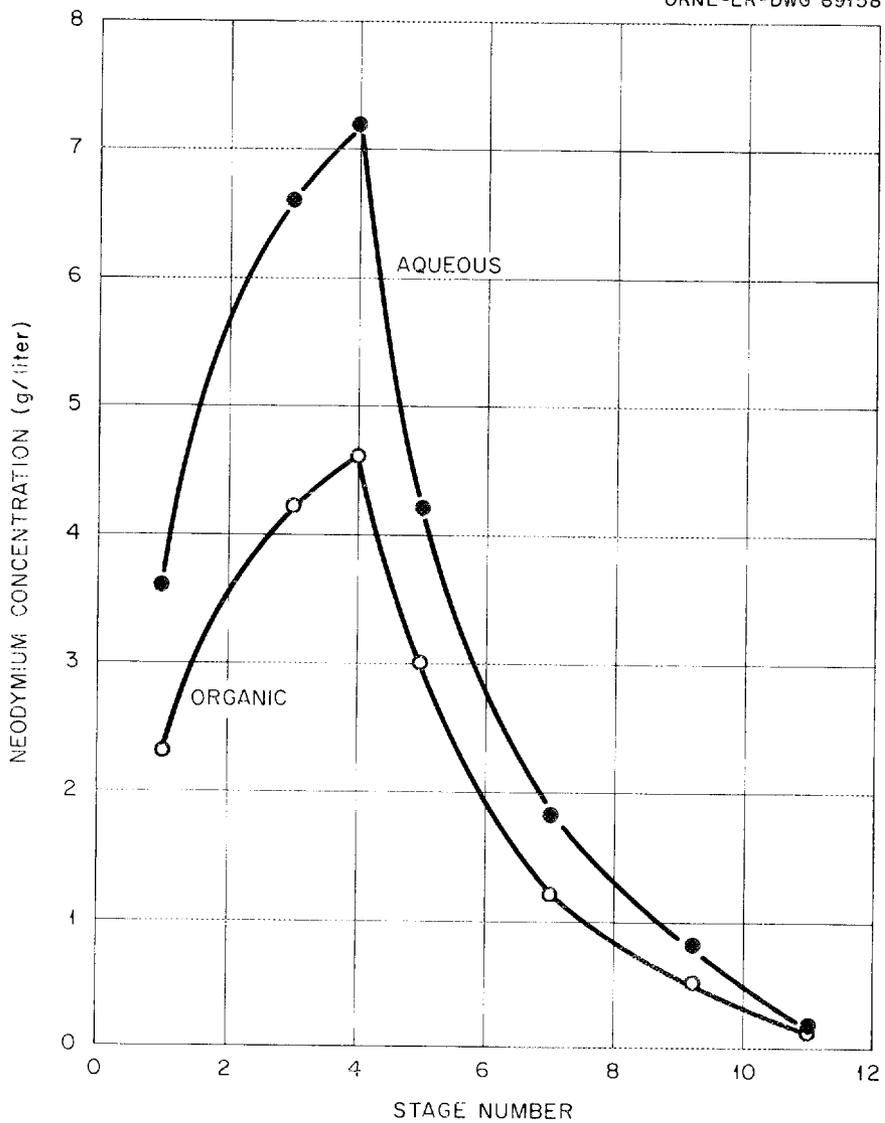


Fig. 1. Concentration Profile of Neodymium in the 11-Stage Mixer-Settler Unit.

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