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BATCH SIMULATION OF RARE EARTHS EXTRACTIVE SEPARATION BY DI (2-ETHYLHEXYL) PHOSPHORIC ACID AND TRIBUTYLPHOSPHATE IN KEROSENE

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ABSTRACT

Liquid-liquid extraction is applied to separate individual rare earths. In this research, 6-stage continuous countercurrent solvent extraction was simulated to extract rare earths from rare earth nitrate solution, which was obtained from monazite processing, to estimate the possible optimum operating conditions for pilot or industrial plants. The solvent(S) per feed(F) ratio (S/F) was varied from 1 to 3. The organic are 1.0 and 1.5 Molars (M) Di (2-ethylhexyl) phosphoric acid (D2EHPA) in kerosene. 50%tributylphosphate (TBP) in kerosene was applied for comparison. It was found that D2EHPA was a good extracting agent for heavy rare earths while TBP extracted well both light and heavy rare earths. After extraction with TBP and D2EHPA, the extraction efficiency at solvent per feed ratio (S/F) = 2 and 3 showed a slight difference. S/F = 2 was selected commercially for operation.

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INTRODUCTION

Rare earths are a relatively abundant group of 17 elements composed of scandium (Sc), yttrium (Y), and the lanthanides. The elements with atomic numbers of 57-63 are light rare earths. The rest including Y are heavy rare earths. In 1990, rare earths were commercially produced by at least 14 countries. The United States was the largest rare-earths producing country, followed with China, Australia, India, and Malaysia. Principal uses of the rare earths are in petroleum fluid cracking catalysts, metallurgical applications, glass polishing compounds, glass additives, permanent magnets, catalytic converter materials, television, lighting, and X-ray intensifying phosphors http://minerals.er.usgs.gov/minerals/pubs/commodity/rare_earths/stat/.

Rare-earths production in Thailand is derived from monazite ore. In 1990, Thailand produced 377 tons of monazite http://minerals.er.usgs.gov/minerals/pubs/commodity/rare_earths/stat/. The monazite processing pilot plant of Thailand or the Rare Earth Research and Development Center (RRDC) was established by the Office of Atoms for Peace, Ministry of Science and Technology, 10 years ago. This Center produces uranium, thorium, and rare earths from monazite ore. Uranium and thorium are starting materials for nuclear fuel production and are reserved for research and development. Rare earths are the only main products that contribute income to support its manufacturing plant and also the uranium-thorium production plant.

For rare earths solvent extraction, the phosphororganic extraction agents, generally used, are either neutral, especially tributylphosphate (TBP), or acidic, mainly di (2-ethylhexyl) phosphoric acid (D2EHPA) (Jedinakova, *et al. 1992*). TBP has been used as the main extractant in the rare earths separation process for a long time. It is the chemicals used in the big rare earths manufacturing companies, i.e. Rhone-Poulenc, Thorium Ltd. (UK) and Indian Rare Earths (Gupta and Krishnomurthy, 1992). Other extractants, which are more expensive, are applied to the smaller production processes. D2EHPA became more important when Peppard (1957), reported that D2EHPA solvent gave a separation factor as high as 2.5 in the chloride and nitrate system, while the highest separation factor in the TBP-HNO_3 system was 1.9.

In 1965, Lenz and Smutz (1966) found that dimerized D2EHPA extracted Sm 40 times faster than monomerized D2EHPA . Imai and Furusaki (1985), and Imai, *et al.* (1987) studied the extraction equilibrium of La with D2EHPA in industrial grade Shellsol-K solvent.. They also studied the extraction rate of La with the same solvent with a stirred transfer cell. Kraikaew, *et al.* (1994) studied the distribution of La and Nd in D2EHPA and TBP. They found that La and Nd were separated better in the HCl-D2EHPA system than HNO_3-TBP system. In 1998, the rare earths research group lead by the Egyptian Nuclear Materials Authority and Atomic Energy Authority. Aly (1998), and Ali, *et al.* (1998) extracted Sm, Eu, Gd and Nd from lanthanide hydrous oxides, which were obtained from Egyptian monazite, with D2EHPA in kerosene.

This work was performed to study solvent extraction of rare earths by 1 M and 1.5 M D2EHPA in kerosene, compared with 50%TBP in kerosene. 6-stage continuous countercurrent liquid-liquid extraction was simulated to study the extraction of rare earths in a pilot plant and an industrial plant. The optimum operating conditions and suitable extractants in the rare earth separation process were also selected.

EXPERIMENTAL PROCEDURE

In this research, rare earths were comparatively extracted from rare earth nitrate solution in dilute nitric acid with 50%TBP in kerosene, 1.0 M and 1.5 M D2EHPA in kerosene. The aqueous system was a nitrate solution, which is less corrosive than a chloride system. The rare earth nitrate feed solution, obtained from monazite processing, was supported from RRDC of the Office of Atoms for Peace. D2EHPA was selected in this research in order to investigate the extraction efficiency compared with TBP, which is the extractant used in the rare earth separation process of RRDC.

The kerosene applied was jet A-1. Jet kerosene is a mixture of liquid hydrocarbons, with a boiling point ranging between 135 and 280°C. A-1 is a commercial name of this jet kerosene. It is obtained from crude oil by distillation and by other technological processes. It is used as fuel for jet aircrafts flying at sonic as well as supersonic speed (http://www.ceskarafinerska.cz/en/catalogue/Jet_Kerosene.asp)

The investigation was performed by batch simulation of continuous countercurrent extraction to reduce operation cost, chemical cost, and operation time (Treybal, 1968). The solvent per feed flow ratios (S/F) was varied as 1, 2, and 3, respectively.

Six-stage continuous countercurrent liquid-liquid extraction was simulated by shaking small batches of feed and solvent in separatory funnels at room temperature (35±1°C). The simulation diagram is shown in Figure 1. Each circle represented a separatory funnel, which, after adequately shaken and the liquids allowed to settle, would be one ideal stage. The amounts of feed and solvent in the flowsheet were made precisely with pipettes. Into the first funnel, the suitable amounts of solvent and feed in the ratio of S/F were placed, then the mixture was shaken, settled and the two phases separated. The shaking conditions were 10 minutes at 200 rpm and the settling time was 10 minutes for two-phase separation.

The simulation was done following the diagram until the products, E_1 and R_6, were obtained. Funnels 1 through 6 in the upper part of Figure 1 represented in every detail the stages of the continuous cascade below. For example, raffinate R_6 from funnel 6 would have all the properties and relative volume of raffinate R_6 of the continuous plant (Treybal, 1986).

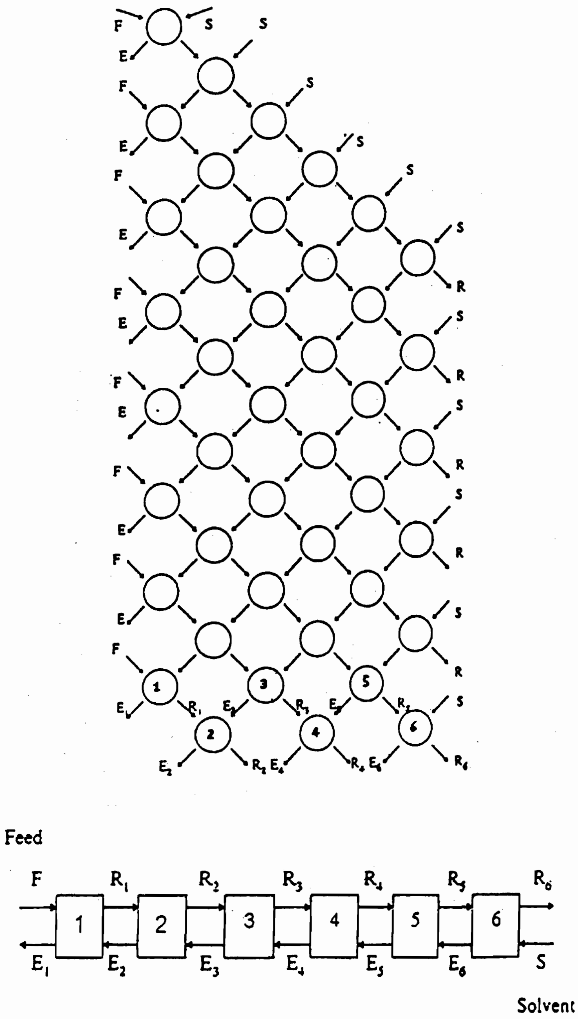


Figure 1 Six-stage countercurrent liquid liquid extraction.
F = Feed solution S = Solvent
E = Extract R = Raffinate
1, 2, 3, 4, 5, and 6 = Stage number

The concentration of each rare earth in the feed solution and raffinates were investigated with ICP-AES (inductive coupled plasma atomic emission spectrometry). Each sample was determined triplicate and the average value was input for the result. Ten rare earths were analyzed at the same time. The percentage of each rare earth in the raffomates and the extraction efficiency were calculated from the following equations.

$$\%\ \textit{rare earths in raffinate} = (C_{i,R}/C_{t,R}) \times 100$$

where, $C_{i,R}$ = Concentration of each rare earth in the raffinate

$C_{t,R}$ = Concentration of total rare earths in the raffinate

$$\%\ \textit{Extraction of each rare earth} = \{(C_{i,F} - C_{i,R6}) / C_{i,F}\} \times 100$$

where, $C_{i,F}$ = Concentration of each rare earth input in the feed solution

$C_{i,R6}$ = Concentration of each rare earth output in raffinate from stage 6

RESULTS AND DISCUSSION

The extraction efficiency of each rare earth as a function of extraction flow rates (S/F) are shown in Figure 2 for the light rare earths, and Figure 3 for the heavy rare earths, respectively. It is found that D2EHPA/kerosene solution, both 1.0 M and 1.5 M, are good extracting agents for heavy rare earths but 50%TBP/kerosene shows better extraction of both light and heavy rare earths. It is also shown that the extraction efficiency of the D2EHPA does not so much depend on the S/F ratio, while there is much difference in the case of TBP. S/F = 1 gives a lower extraction efficiency than S/F = 2 and S/F = 3.

Percentages of rare earths in raffinate output from stage 6 as a function of extraction flow rates (S/F) are illustrated in Figure 4 and Figure 5 for the light rare earths and the heavy rare earths, respectively. Percentages of rare earths in raffinate are low except La and Nd. However, percentages of La and Y in raffinate are higher when 50%TBP/kerosene are applied as a solvent. D2EHPA/kerosene shows a lower extraction efficiency for the remaining rare earths because of the higher percentages in raffinate output.

Figure 6 and Figure 7 show the extraction efficiency of each rare earth when using various extraction agents at S/F = 2 and 3. It is shown that the 50%TBP in kerosene solution is the better extracting agent for the light rare earths than the D2EHPA in kerosene solution. However, the extraction efficiency of both TBP and D2EHPA is nearly the same for the heavy rare earths including Y. In other words, both TBP and D2EHPA are good extracting agents for heavy rare earths.

The result also show that the extraction efficiency is not so different when using S/F = 2 and 3. Therefore, it is suggested to use S/F = 2 for the extraction of rare earths with either TBP or D2EHPA in kerosene. The amount of solvent can be saved and the operation cost will be reduced.

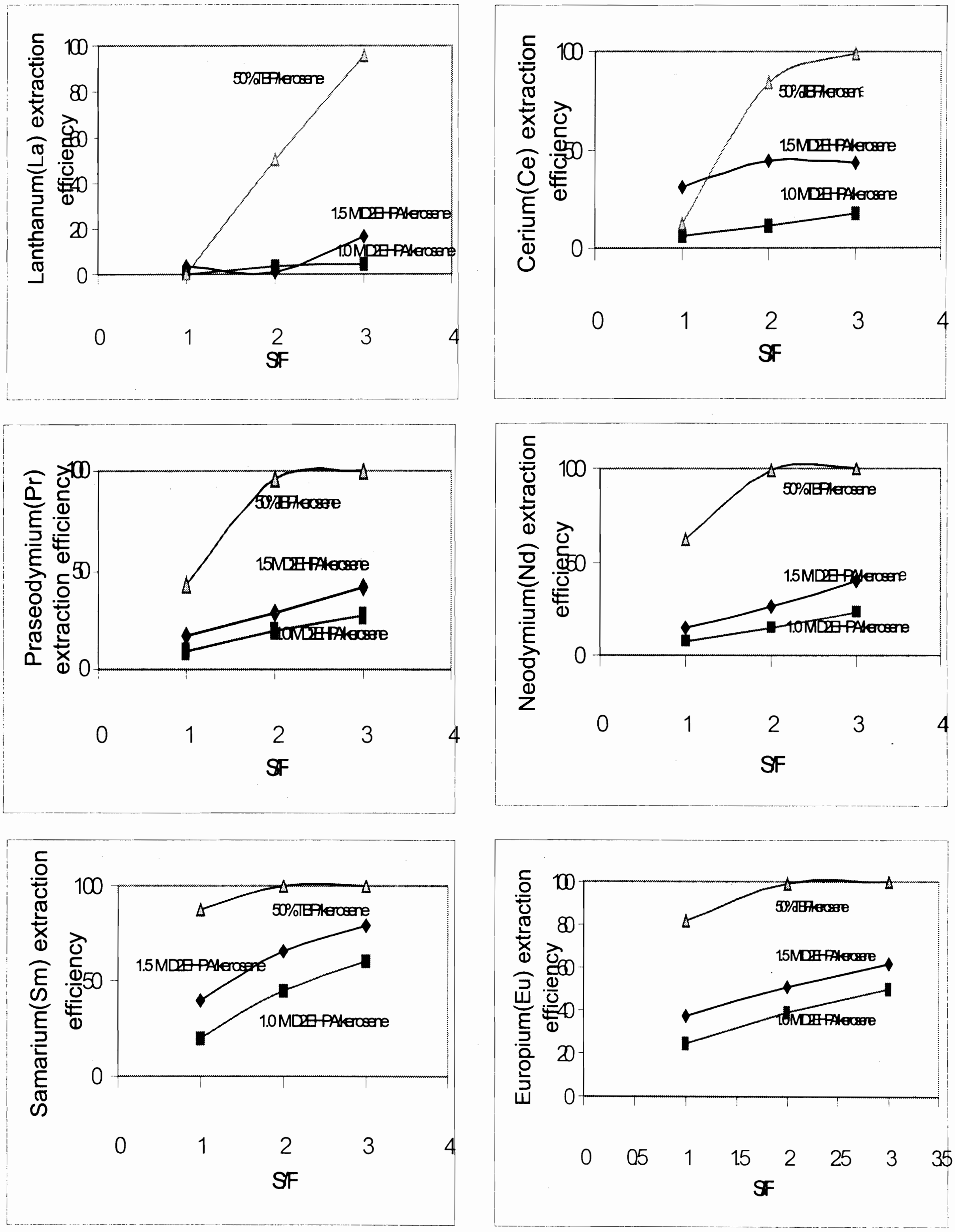


Figure 2 Extraction efficiency of each light rare earth (La, Ce, Pr, Nd, Sm, and Eu) as a function of extraction flow rate (S/F).

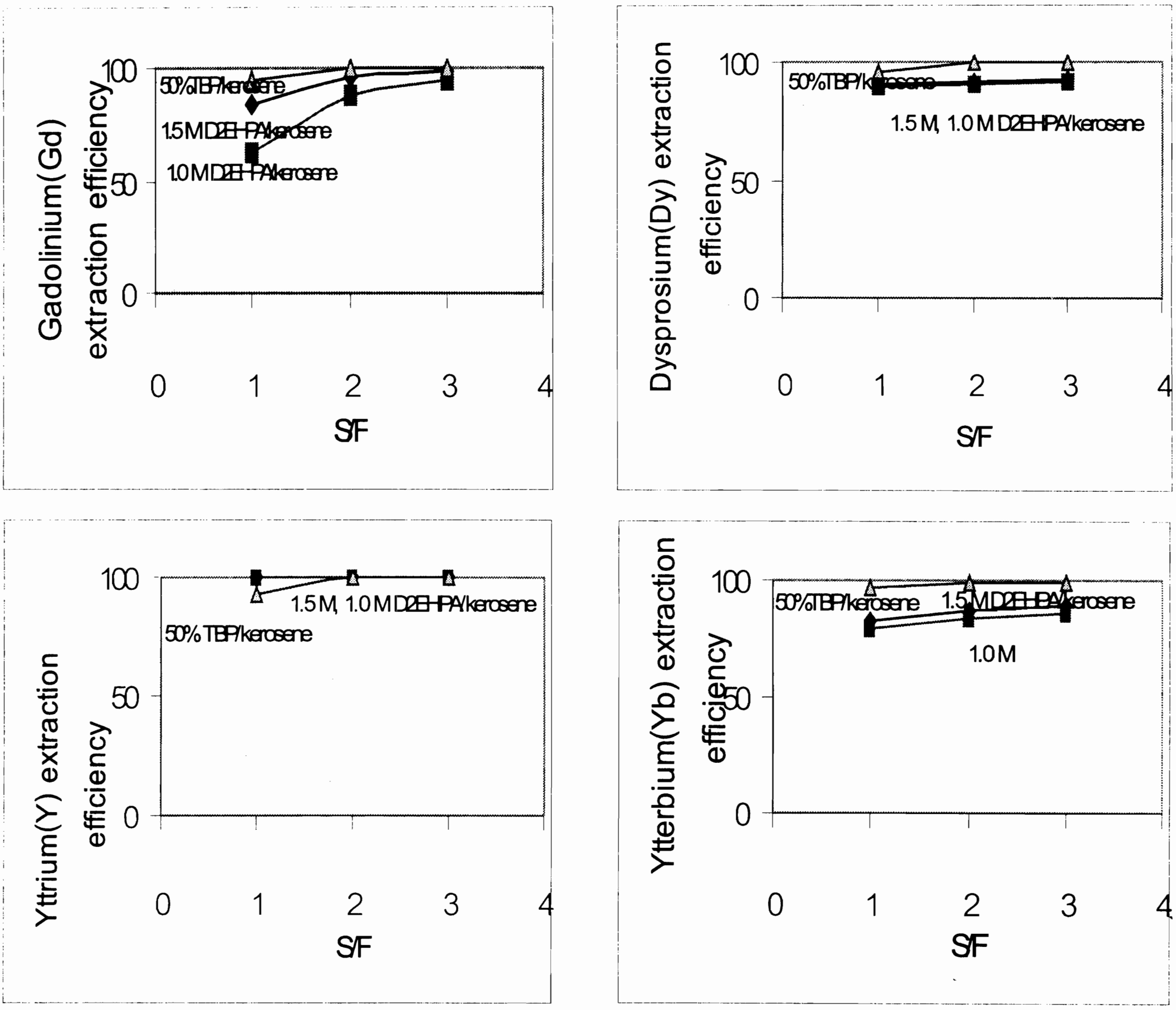


Figure 3 Extraction efficiency of each heavy rare earth (Gd, Dy, Yb, and Y) as a function of extraction flow rate (S/F).

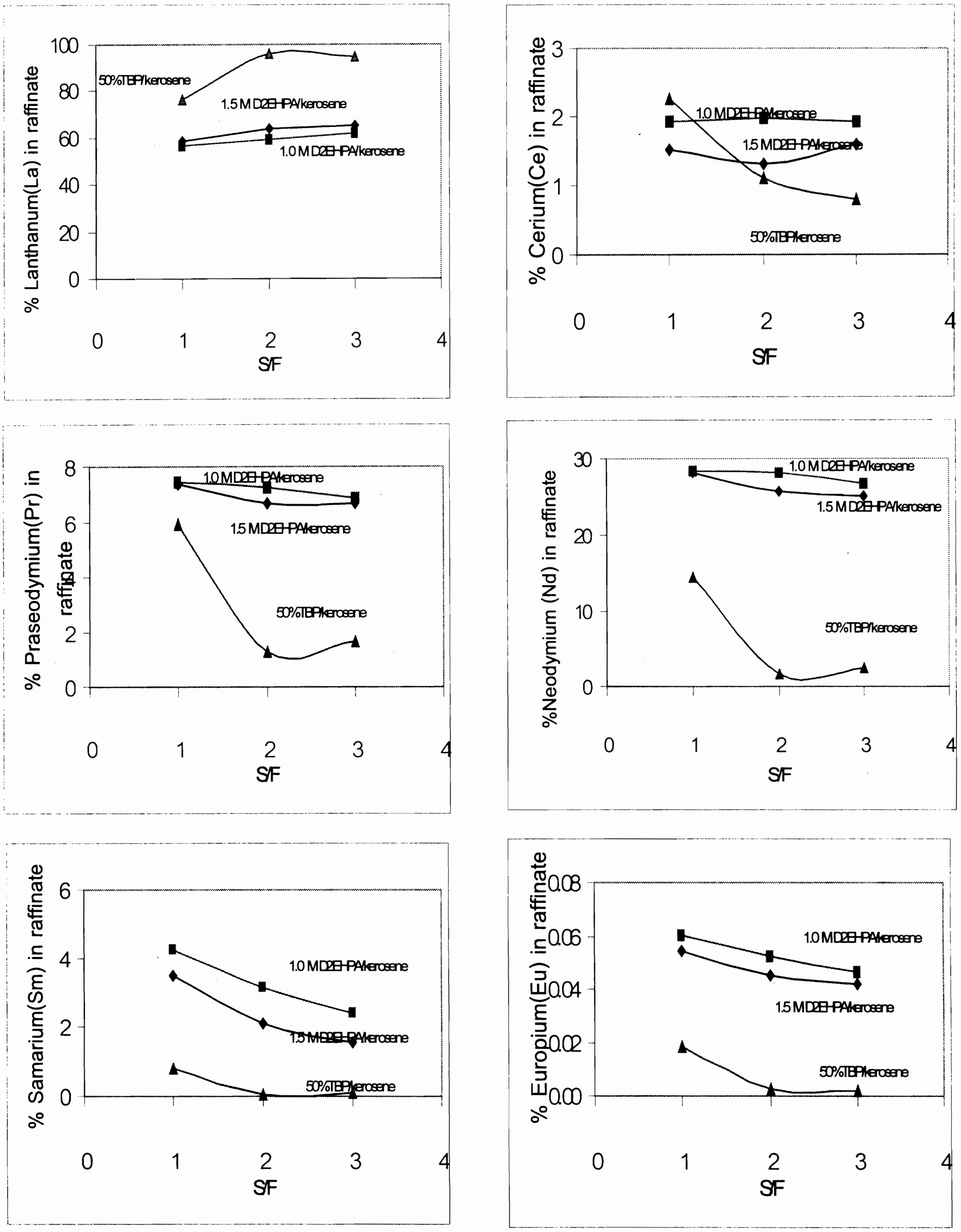


Figure 4 Percentage of each light rare earth (La, Ce, Pr, Nd, Sm, and Eu) in the raffinate from stage 6 as a function of extraction flow rate (S/F).

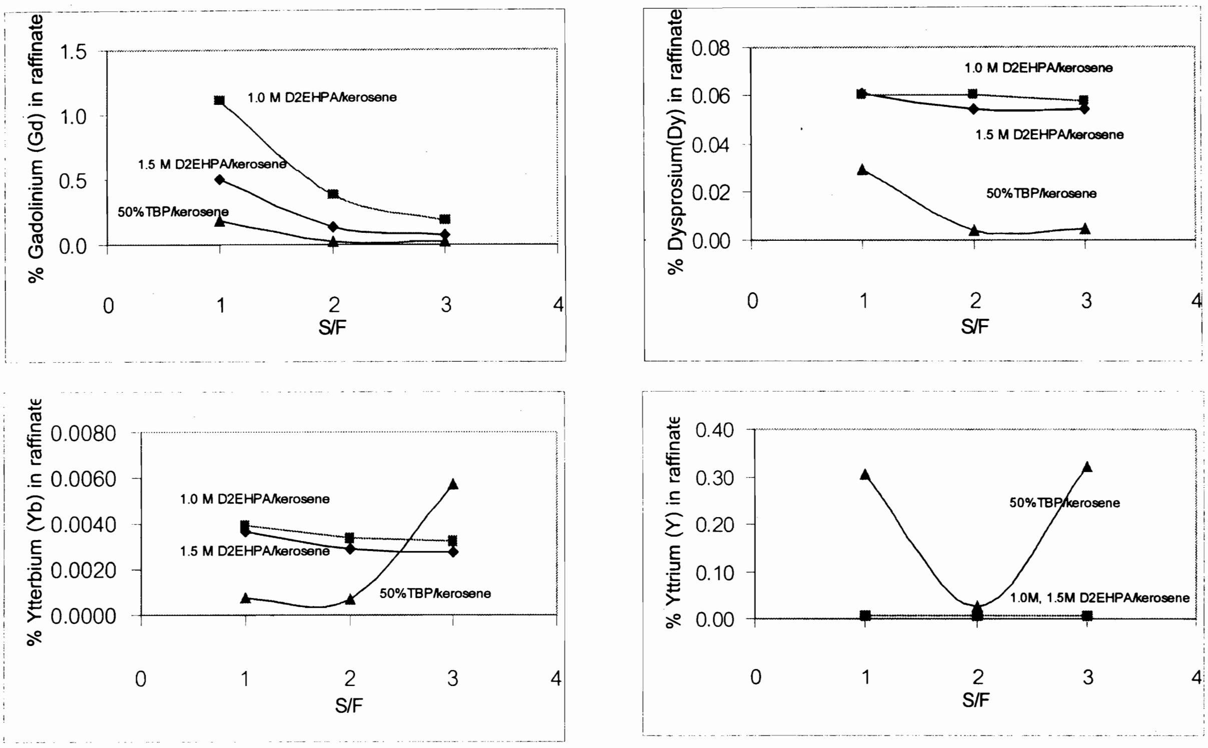


Figure 5 Percentage of each heavy rare earth (Gd, Dy, Yb and Y) in the raffinate from stage 6 as a function of extraction flow rate (S/F).

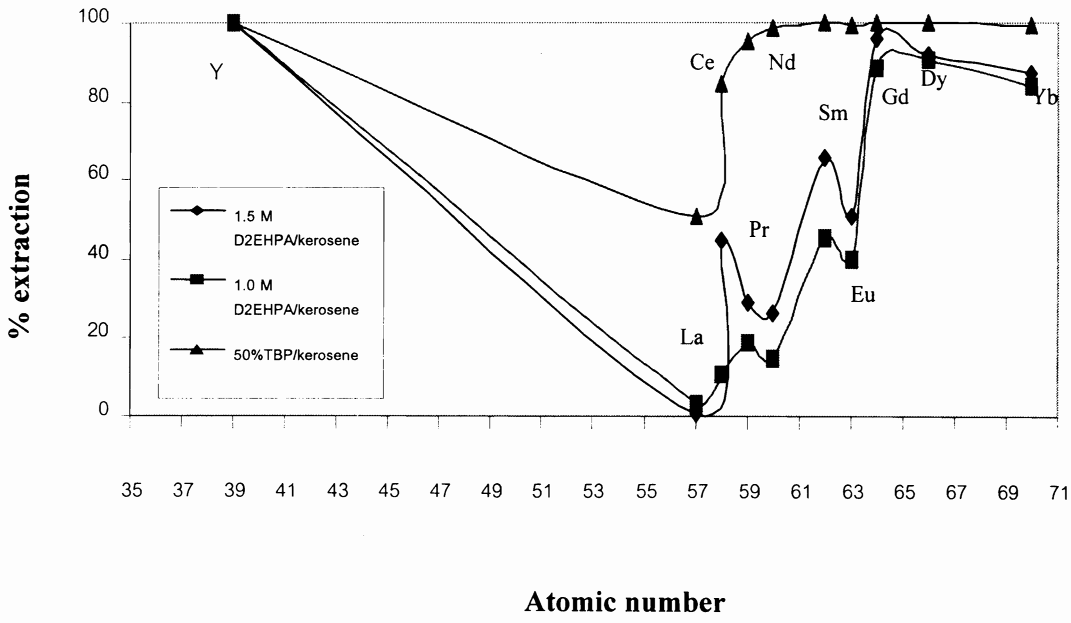
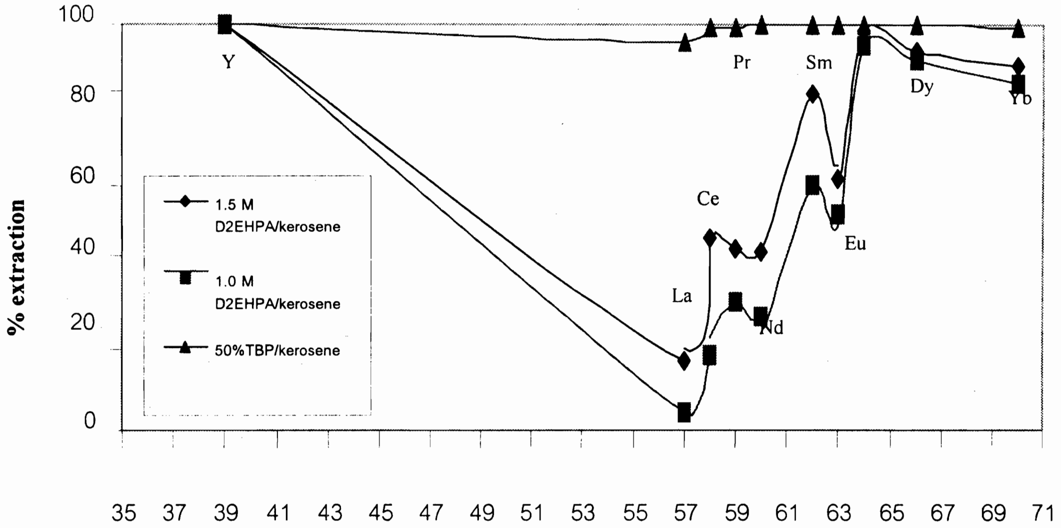


Figure 6 Rare earth extraction efficiency of each extracting agent when using solvent per feed ratio = 2.



Atomic number

Figure 7 Rare earth extraction efficiency of each extracting agent when using solvent per feed ratio = 3.

CONCLUSIONS

TBP can extract light and heavy rare earths satisfactorily but D2EHPA is a good extracting agent for La and heavy rare earths. 1.0 M D2EHPA/kerosene is more suitable commercially than 1.5 M D2EHPA/kerosene. However, there is no commercial rare earth separation process in Thailand using D2EHPA as the extractant.

For commercial operations using 50%TBP/kerosene, S/F = 2 is more economical because of the similar results to S/F = 3. Solvent cost and treatment cost can be saved. La is enriched to 95.9% in raffinate from 51.6% in rare earth nitrate feed solution. Therefore, for $RE(NO_3)_3$/dil HNO_3 - 50%TBP/kerosene system, La will be the main rate earth separated to raffinate while the rest of the rare earths remain in the organic phase.

If these optimum conditions work satisfactorily in the pilot plant, it is possible to produce individual rare earths with required specification. The income from rare earth sales can support its production plant and also the uranium-thorium plant.

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