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OF SAMARIUM AND GADOLINIUM

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ABSTRACT

The present work was aimed at investigating the separation of two rare-earth elements, samarium-gadolinium, through solvent extraction. A comparative study, in batch and in continuous scale, has been carried out with a phosphoric acid (D2EHPA), a phosphonic acid (IONQUEST 801) and a phosphinic acid (CYANEX 272) extractant. Efficient Samarium-Gadolinium separation has been achieved with the phosphoric and the phosphonic extractants.

INTRODUCTION

The interest concerning rare earths in the international market is due to the widespread use of these elements, which in high purity separate form may cost several times more than in a mixed state [1].

Countries such as France and Japan, which do not have major reserves of rare earth minerals available, have mastered the technology of fractionation and purification and dominate, together with the United States, world trade in these elements. More recently China has also come to hold sway over a significant portion of the aforesaid market, mainly on account of possessing the largest known reserves.

In the Fifties, Brazil achieved a prominent position in the world market for rare earth oxides. Neverthless, progress remained practically at a standstill, in view of the outstanding evolution in the technology of separation and application of the isolated elements that was achieved in other countries. The situation is currently being inverted, with considerable interest being displayed in the development of the industrial process for obtaining the rare earth elements in separate form. A number of research activities have gotten under way for that purpose.

Of the elements belonging to the lantanide series, gadolinium is of particular importance to the nuclear industry. On account of its broad impact cross section for absorption of neutrons, it is used to control nuclear chain reactions in nuclear power reactors.

In addition to this, the development of the samarium-cobalt permanent magnet, with flux density far higher than that of similar products already available, has turned samarium into an industrial material of outstanding significance.

The separation of rare-earth elements, such as samarium and gadolinium, is usually carried out with organophosphorus extractants, D2EHPA (di 2-ethyl-hexyl phosphoric acid) being the most used. More recently, processes based on phosphonic acid extractants have been successfully applied to the separation of these elements. Phosphinic acid extractants show also good perspectives of commercial applications.

Even though some published papers compare the efficiency of organophosphorus extractants for the separation of rare earth elements, only a few mention process conditions obtained from continuous operation [2,3]. The main purpose of the present investigation is to compare the results in the separation of samarium and gadolinium using three organophosphorus extractants: D2EHPA (Di-2-ethylhexyl phosphoric acid), EHEHPA (2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester) and DTMPPA (Di-2,4,4-trimethylpentyl phosphinic acid). The experiments were conducted in a continuous mixer-settler unit.

This study is part of a broader investigation aimed at defining process conditions to separate the heavy rare-earth constituents of a monazite concentrate processed by Nuclemon Co.

Reagents and Solutions

The aqueous feed solution was prepared from samarium and gadolinium oxides (99.9% Sm_2O_3 or Gd_2O_3) supplied by Rhône-Poulenc, Inc. Those oxides were dissolved in a solution of HCl and the final acidity was adjusted to the required conditions. Concentrations of 25 g/l of Sm_2O_3 and 12 g/l of Gd_2O_3 were chosen, based on the expected liquor composition to be industrially processed. Analytical reagent grade and distilled water was used throughout the experiments.

The organic solution was prepared with the following extractants:

- D2EHPA (DP-8R)-Di-2-ethylhexyl phosphoric acid, supplied by Daihachi, Chemical Industry Co, Ltd.
- EHEHPA (Ionquest 801) - 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester, supplied by Albright & Wilson Americas, Inc.
- DTMPPA (CYANEX 272) - Di-2,4,4-trimethylpentyl phosphinic acid, supplied by American Cyanamid Co.

Those extractants were diluted in n-dodecane of high purity.

Preliminary batch tests were carried out in order to investigate the conditions which most affect samarium and gadolinium extraction and their separation factors, such as pH in the aqueous phase, phase ratio (O/A) and contact time.

The equilibrium data compiled in the previous experiments were fed to a thermodynamic model [4]. Taking into account the desired

recovery, the model calculated process variables such as: number of stages, phase ratios, feeding point and others.

Continuous extraction and scrubbing tests were run on a micro-pilot solvent extraction unit. That unit consists of a battery of compacted mixers and settlers with 16 stages and a single drive system. The volumes of the mixing and settling chambers are 12.5 cm^3 and 50 cm^3 respectively, and each stage has independent interface control. The feed flow was maintained at approximately 350 cm^3/h.

Figure 1 shows a schematic flowsheet of the 12 stages used for extraction and scrubbing.
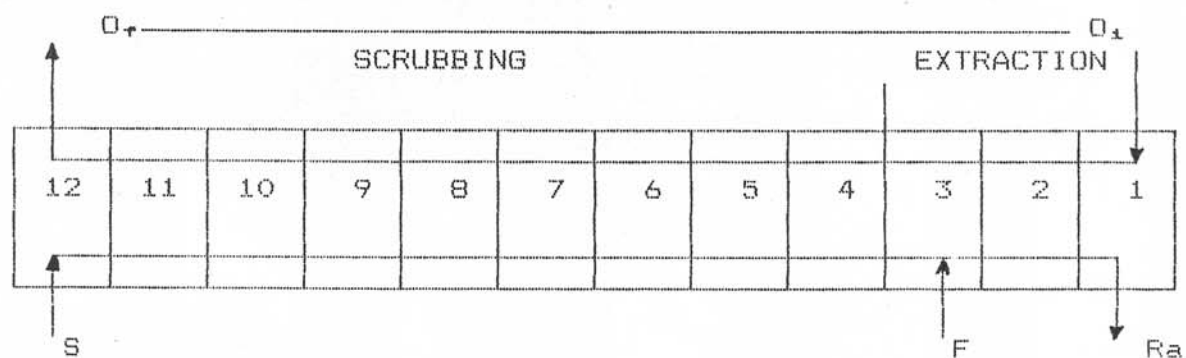
O_i-Organic feed; O_r-Loaded Organic; F — Aqueous feed; Ra — Raffinate; S — acid scrubbing solution.

Fig.1 — Schematic Extraction & Washing Process Flowsheet

To ensure the stability of the operation, the flow rates of the aqueous and organic phases were monitored at thirty-minute intervals, through an on-line metering system.

Sampling of the outlet products, the raffinate (Ra) and the loaded organic (Of), were also effected at thirty minute intervals for chemical analysis purposes. At the end of the tests samples were taken from each stage.

X-ray energy spectrometer (KEVEX), and the molecular absorption spectrometer were used to determine the rare earth concentrations in the aqueous phase.

RESULTS AND DISCUSSION

Preliminary Batch Experiments

Figure 2 shows the extraction of samarium and gadolinium as a function of the initial pH of the aqueous phase, for the three extractants tested. It can be observed that D2EHPA is a more effective extractant, as compared to EHEHPA and DTMPPA, for both Gadolinium and Samarium. Highest separation factors are also obtained with D2EHPA, as indicated by Figure 3. The separation factor, O Gd-Sm is defined as the ratio between the extraction coefficients of gadolinium and samarium, respectively.

The extraction reaction may be described by Eq. (1):

$$Re^{3+}_{(aq)} + 3(HX)_{2(org)} = ReX_6H_{3(org)} + 3H^+_{(aq)}$$

(1)
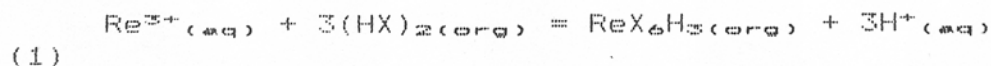
where Re represents the rare-earth elements, $(HX)_2$ refers to the dimeric form of the organophosphorus extractants and (aq) and (org) represent the species in the aqueous and organic phase, respectively.

Equation (1) shows that with increasing acidity, the reaction is shifted preferentially to the stripping direction. This trend explains the low extraction ratios obtained in the lower pH region, as shown in Figure 2. Furthermore, the small effect of the initial pH on the metals extraction and on the separation factors is also explained by the change in acidity that takes place as the reaction proceeds, specialy in the presence of the phosphonic and phosphinic extractants.

With a view to diminish the variation of pH caused by the extraction reaction, saponification of EHEHPA and DMTPPA was carried out. This saponification is made through pre-equilibrating the solvent with an ammonium hydroxide solution.

Figure 4 shows the influence of the equilibrium acidity, on the extraction of samarium and gadolinium. It can be noticed that the extraction diminishes substantially with increasing acidity (or decreasing pH) for all the three extractants. The effect is more pronounced for the phosphonic and mainly, for the phosphinic reagent. The results indicate that for a effective extraction of the two rare-earth elements in a HCl medium, the acidity must be carefully controlled at the following levels:

    D2EHPA   — 0.1 to 1.0 N
    EHEHPA   — 0.05 to 0.3 N
    DMTPPA   — 0.01 to 0.02 N.

D2EHPA can be used in its original form, since the variation of acidity during the extraction is not sufficient to change the conditions required for an adequate extraction of the two rare-

earth elements. EHEHPA and DMTPPA, on the other hand, have to be previously saponified in order to maintain the required acidity level. The acidity ranges levels found in the present work are in agreement with reported data obtained with EHEHPA and DMTPPA by other investigators [3,4].

Figure 5 show the separation factors as a function of the equilibrium acidity. The parameters obtained under the most favourable experimental conditions are:

D2EHPA - 3.8

EHEHPA - 3.7

DMTPPA - 2.3.

After defining the most adequate conditions for Sm-Gd separation, kinetics studies have been carried out. Equilibrium is attained after two minutes with D2EHPA, whereas with the other two extractants after three minutes.

Continuous Experiments

The design of an extraction system for the separation of rare earth elements requires the knowledge of process conditions such as: feed composition, number of stages, feed stage, phase ratio, acidity of scrub solution and others. The effect of the above mentioned variable on the recovery and purity of the components to be separated may be predicted through the development of a mathematical model based on the extraction reaction (Eq.1). There is a considerable number of published papers on modelling of rare earths separation by counter-current extraction [4,5,6,7,8].

Silva [4] used equations that describe the mass balance of each component in each stage, equilibrium data and the ionic balance in aqueous phase to develop a model that predicts the yield and purity of products. In the present work, the model developed by Silva was applied to the data obtained in the batch tests in order to define the initial operation parameters to be used in the continuous mixer-settler units.

During the course of this investigation minor adjustments were made in the feed ratio (O/A), acidity of scrubbing solution, number of stages and feed stage, as a function of the results achieved in the previous experiment. The conditions were varied in quest for maximum efficiency of separation so as to maximize the purity of gadolinium and samarium in the organic phase and in the raffinate, respectively.

Tests with D2EHPA

In the tests with D2EHPA, the variable that displayed the most significant effect was the acidity of the scrubbing solution. Three experiments were run, varying the concentration of HCl in that solution, at the following levels: 0.75, 0.90 and 1.0 N. The remaining conditions, as established in the previous experiments (Table 1), were maintained constant.

Table 1 - Experimental Conditions for the Sm/Gd Separation
using D2EHPA

Stage	Extraction	Scrubbing
Number of stages	3	9
Phase ratio (O/A)	1/1	3/2
Retention time (min)	2.5	3.0

Figure 6 shows the final concentration profiles for samarium and gadolinium in the unit. It will be noted that the increase in the acidity of the aqueous phase led to a reduction in the extraction of samarium, and greatly improved the separation of the elements. In the scrubbing stages, the concentration of samarium diminishes rapidly while that of gadolinium tends to remain constant. In the 2nd. and 3rd. runs the concentration curves of these elements cross one another, meaning that the condition of higher acidity favors selective stripping of samarium.

The experimental conditions adopted in the 3rd. test (Table 1, acidity 1.0 N), were the most favorable for the separation of samarium and gadolinium. The samarium product (raffinate) reached a purity and a yield of 97%. The gadolinium product (loaded organic) attained a purity of 93.2% and a yield of 92%.

Tests with EHEHPA

The experimental conditions of the tests with phosphonic acid were also oriented by the results obtained under batch conditions. As already mentioned, saponification of this

extractant plays a fundamental role in the efficiency of separation of the rare earth elements. An intensive study of this process variable was made until it became possible to attain a satisfactory condition, meaning that the pH of the raffinate solutions had to be maintained between 0.5 and 1. The experimental conditions that led to the best results are shown in Table 2.

Table 2 - Experimental Conditions for Sm/Gd Separation
Using EHEHPA

Stage	Extraction	Scrubbing
Number of stages	7	5
Phase ratio (O/A)	4/3	2/1
Retention time (minutes)	2.5	2.5
Acidity of scrubbing solution	-	0.5 N

Figure 7 indicates the concentration profiles for samarium and gadolinium, considering the various stages, under conditions shown in Table 2. It is important to note the differences in the profiles obtained with D2EHPA and EHEHPA. With the phosphonic acid, the extraction appeared to be more selective, in spite of showing lower separation factors as compared to D2EHPA. The concentration of Samarium in the organic phase decreased from the first stage (1.E.) to the last stage, as a result of the scrubbing effect of the acid solution. The same behaviour occured in the aqueous phase, i.e., there was also a decrease in Samarium concentration from stage 2-E to stage 12-E. In stage 1-E

Samarium was strongly extracted as the rich Samarium aqueous phase was contacted with fresh solvent.

The concentration of Gadolinium increased in both phases from stage 1-E until stage 7-E and started decreasing after that, as a result of the scrubbing effect of the acid solution. Though this solution was used to scrub Samarium, it also removed Gadolinium.

Whereas in the process using D2EHPA, there was practically no transfer of gadolinium to the aqueous phase in the scrubbing stages, in the process using EHEHPA there was a slight removal of this element, even when very low acidity was used.

The products of samarium and gadolinium obtained with the phosphonic acid extractant displaed degrees of purity exceeding 92% and 98% respectively. Separation yields were 99% for samarium, and 83% for gadolinium.

Tests using CYANEX 272

It was not possible to attain a satisfactory operational condition for the separation of samarium and gadolinium using this extractant. The range of acidity that must be maintained for a efficient separation is extremely low and narrow, calling for controls more sensitive than those available. When a certain level of acidity was exceeded, there was practically no extraction and if that level of acidity diminished, an emulsion formed as a result of precipitation of the elements.

Continuous Extraction-Scrubbing-Stripping Tests

Once the optimum conditions of extraction and scrubbing using D2EHPA and EHEHPA had been defined, the complete extraction, scrubbing and stripping circuit was set up.

In the tests, five different stages of stripping were defined, and a feed ratio (O/A) = 5. The concentration of HCl in the stripping solution varied from 2 to 5 N of HCl.

Stripping yields of 100% were attained for both reagents, but with quite a significant difference. For the stripping of the rare earth elements from D2EHPA, 5 N hydrochloric acid solution was employed whereas in the case of the EHEHPA, the acid concentration was maintained at 2 N. Since the stability of the metal-D2EHPA complex is higher than that for the metal-EHEHPA complex, stripping of the rare earth elements was a more favorable when phosphonic acid was used [9].

CONCLUSIONS

The results showed that both D2EHPA and EHEHPA can be effectively used to separate samarium and gadolinium from hydrochloric acid solutions.

The advantages displayed by D2EHPA as compared to EHEHPA refer to the possibilities of using a lower feed ratio (O/A) and a reduced number of stages. On the other hand, the use of EHEHPA proved to

be more favorable in the stripping stage, permitting use of a more dilute HCl solution.

Using DTMPPA, it was not possible to attain a satisfactory operational condition for the Samarium-gadolinium separation.

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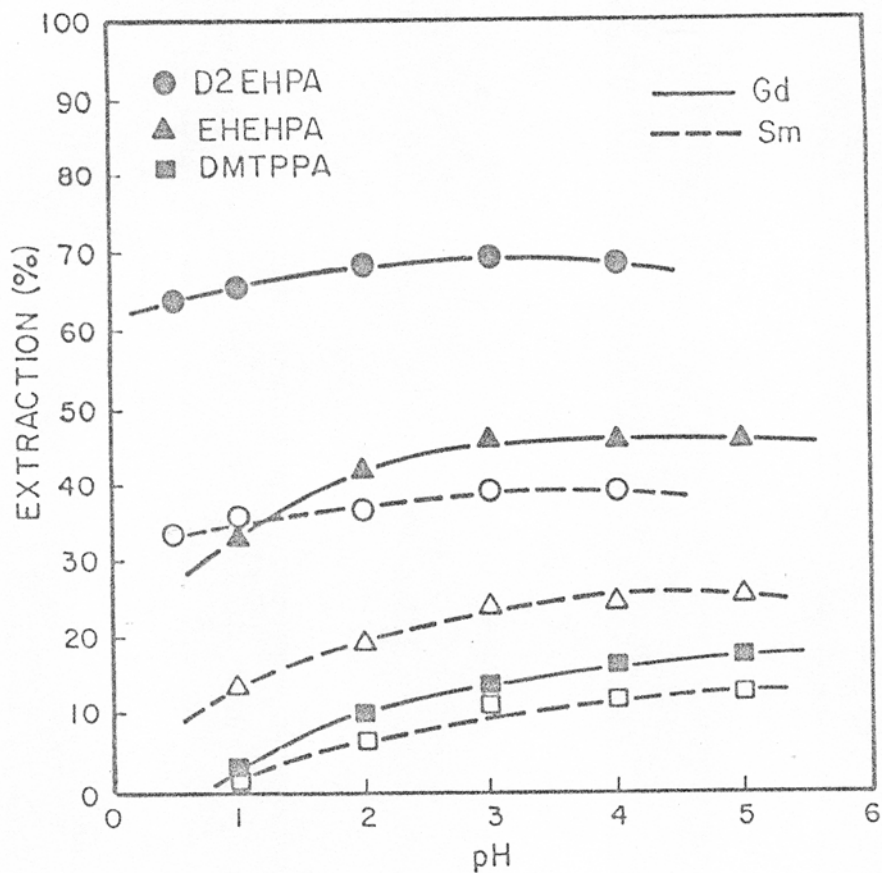
FIG. 2 - EFFECT OF THE INITIAL pH IN THE SAMARIUM AND GADOLINIUM
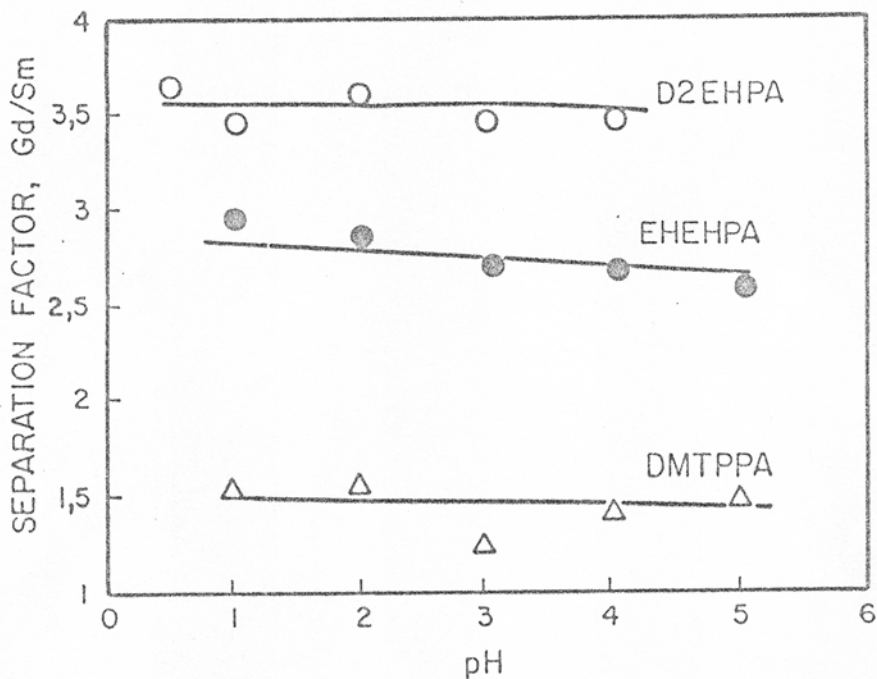EXTRACTION WITH VARIOUS EXTRACTANTS

FIG. 3 - EFFECT OF THE INITIAL pH IN THE SEPARATION FACTOR (Sm/Gd)
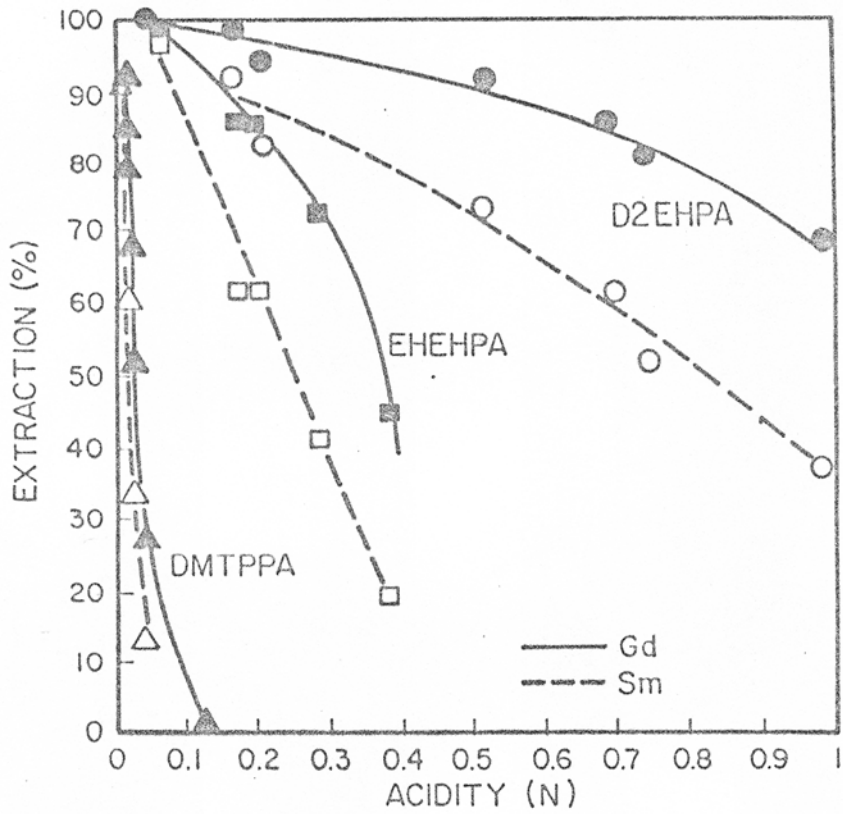WITH VARIOUS EXTRACTANTS

FIG. 4 - EFFECT OF EQUILIBRIUM ACIDITY IN THE SAMARIUM AND GADOLINIUM
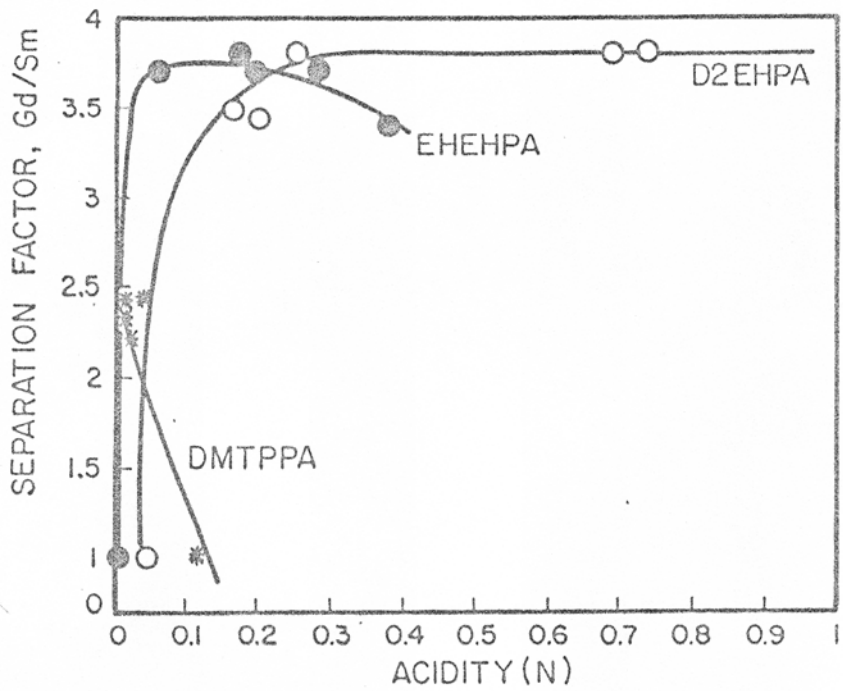EXTRACTION WITH VARIOUS EXTRACTANTS

FIG. 5 - EFFECT OF EQUILIBRIUM ACIDITY IN THE SEPARATION FACTOR (Sm/Gd)
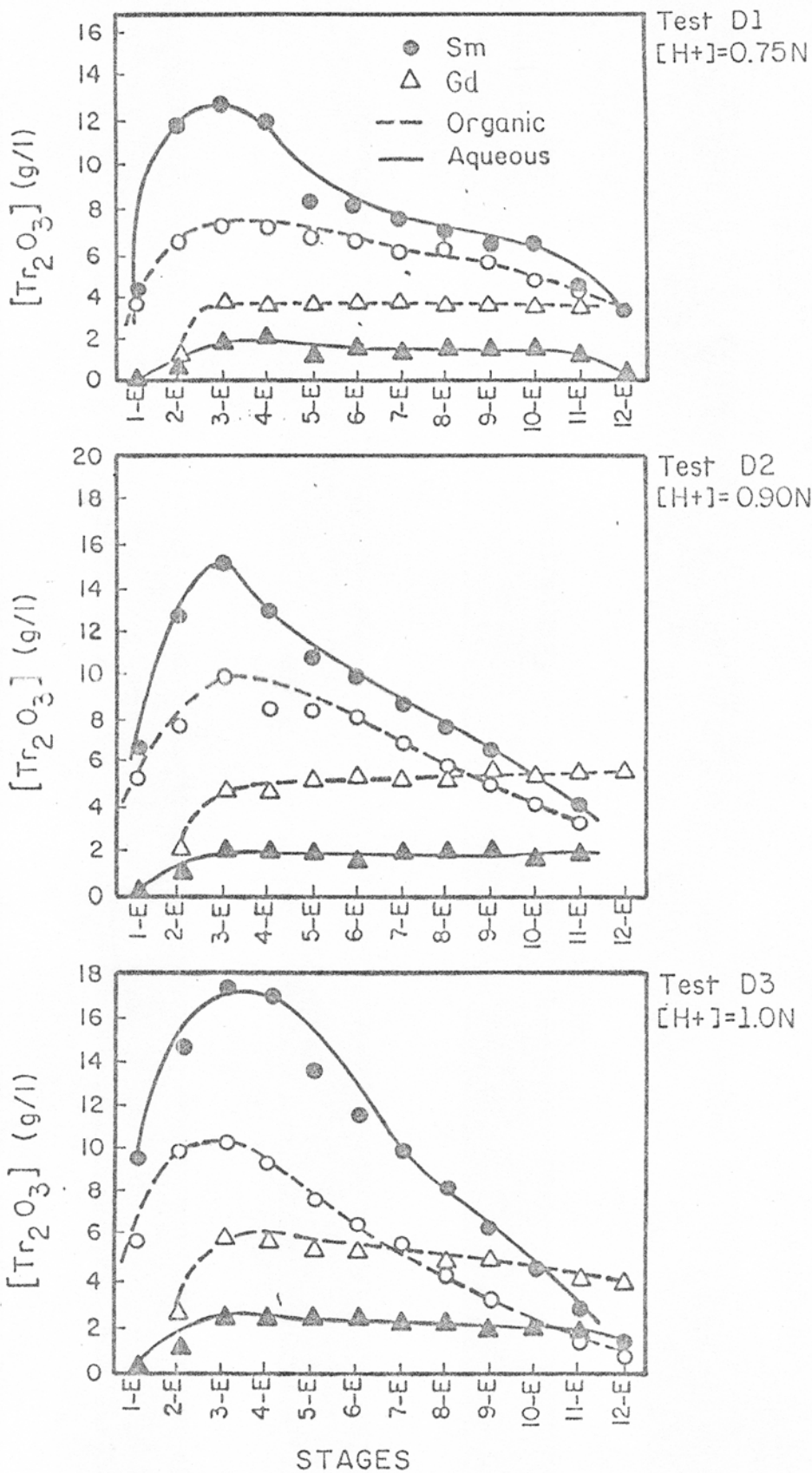WITH VARIOUS EXTRACTANTS

FIG. 6 — SAMARIUM AND GADOLINIUM CONCENTRATION PROFILE CONSIDERING THE VARIOUS STAGES OF EXTRACTION-SCRUBBING RUNS WITH D2EHPA
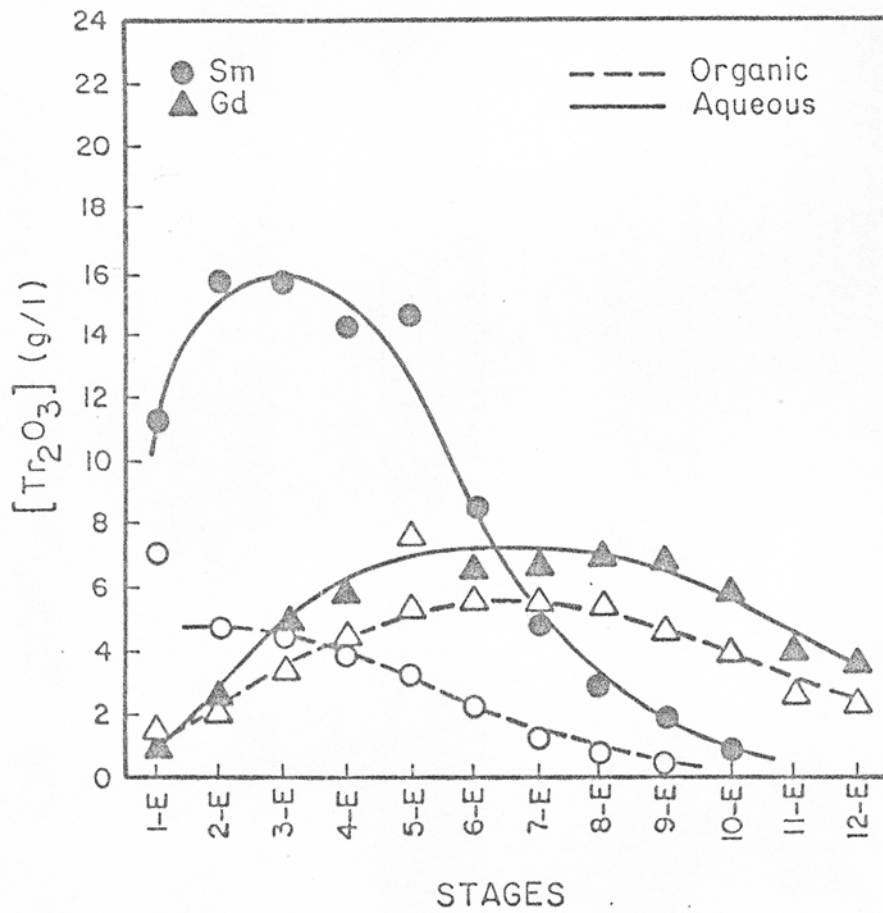
FIG. 7 - SAMARIUM AND GADOLINIUM CONCENTRATIONS PROFILE CONSIDERING THE VARIOUS STAGES OF EXTRACTION-SCRUBBING RUNS WITH EHEHPA